

Nonvolatile Residue Solvent Replacement

1 March 1995

Prepared by

G. S. ARNOLD and J. C. UHT
Mechanics and Materials Technology Center
Technology Operations
Engineering and Technology Group



Prepared for

SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE MATERIEL COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245

Programs Group

19950926 093

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-93-C-0094 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Suite 6037, Los Angeles AFB, CA 90245-4687. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein Principal Director, Mechanics and Materials Technology Center. Lt James R. Schorie was the project officer.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



JAMES R. SCHORIE, LT, USAF
Manager, Environmental Programs

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1 March 1995		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE Nonvolatile Residue Solvent Replacement				5. FUNDING NUMBERS F04701-93-C-0094	
6. AUTHOR(S) Arnold, Graham S., and Uht, Joseph C.					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Aerospace Corporation Technology Operations El Segundo, CA 90245-4691				8. PERFORMING ORGANIZATION REPORT NUMBER TR-95(5448)-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Space and Missile Systems Center Air Force Materiel Command 2430 E. El Segundo Blvd. Los Angeles Air Force Base, CA 90245				10. SPONSORING/MONITORING AGENCY REPORT NUMBER SMC-TR-95-28	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Control of contamination during processing and integration of spacecraft and launch vehicles is fundamental to ensuring mission performance and longevity. Molecular contamination, or nonvolatile residue (NVR), is limited by selection of materials and the control of procedures and facilities. Tests to diagnose NVR accretion in clean rooms and on spacecraft surfaces rely on toxic and ozone-depleting solvents (methylene chloride and 1,1,1 trichloroethane). This report documents literature review and laboratory experimentation to identify a replacement for these undesirable materials. Two clear candidates for a replacement NVR solvent emerge from the testing reviewed and reported here: ethyl acetate and ethyl acetate/cyclohexane azeotrope. For laboratory operations that must rely on procuring high purity solvents, pure ethyl acetate is recommended. For large laboratories that are equipped to purify their own solvents, the mixture is a good option.					
14. SUBJECT TERMS Contamination Methylene Dichloride 1,1,1 Trichloroethane Dichloromethane Nonvolatile Residue Ethyl Acetate Ozone Depleting Chemicals				15. NUMBER OF PAGES 73	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
20. LIMITATION OF ABSTRACT					

Acknowledgements

This work was supported by the United States Air Force Space and Missile Systems Center (SMC) under contract number F04701-93-C-0094. The authors wish to acknowledge the assistance of Mr. Rory Tabatt and Mr. Barry Sinsheimer in the early stages of laboratory work and useful discussions with Mr. Eugene Borson and Ms Gloria To.

Ms. Elizabeth King, Dr. Tom Giordano, and Dr. Russ Barrows of the Martin Marietta Corporation were generous in sharing their results and thoughts on this problem. Mr. Andreas Parks, of Lockheed Missiles and Space Co., communicated significant and helpful results. Insight into the issues of solvent replacement was also provided by Ms Elizabeth Hill and Mr. Kenneth Monroe, of the Research Triangle Institute. This open communication over the issues of NVR solvent replacement for USAF applications is producing a growing consensus on the proper approach to follow.

The authors are grateful for the support and encouragement of Mr. Norman Keegan, Mr. Noble Dowling, and Dr. Thomas Spiglanin, of the Aerospace Corporation and Mr. John Edwards of the USAF SMC.

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Contents

Acknowledgements	iii
Figures	vii
Tables	viii
Acronyms and Abbreviations	ix
1.0 Introduction	1
2.0 Titan Program NVR Solvent Usage	3
2.1 WR Contamination Control Plan	3
2.1.1 Referenced Documents	3
2.1.2 Payload Fairing Processing Facility/Clean Work Area (PLFPF/CWA)	3
2.1.3 Clean Enclosure	3
2.1.4 Appendix C- Optional Services	3
2.1.5 Appendix D- Titan IV Payload Fairing Contamination Control Plan	4
2.2 ER Contamination Control Plan	4
2.2.1 Referenced Documents	4
2.2.2 Payload Fairing Processing	4
2.2.3 Appendix C- Additional Services	4
2.2.4 Upper Stage Contamination Control Plans	4
3.0 Solvent Screening	5
3.1 Solvent Properties Screening	6
3.2 Vapor Pressure Analysis	11
3.3 Hazard Evaluation	13
3.4 Screening Summary	15
4.0 Review of Relevant Testing Results	19
4.1 Martin Marietta CCAS Testing	19
4.2 Martin Marietta PJKS Testing	21
4.3 Lockheed Missiles and Space Corporation Testing	23
4.3.1 Summary of Results	23
4.3.2 Hansen Parameter Evaluation of LMSC Solvents	23
4.3.3 Comments on the Use of Cyclohexane/Ethyl Acetate Azeotrope	28
4.4 NASA Marshall Space Flight Center Testing	29
4.5 CFM Technologies Testing	30
4.6 Aqueous NVR Determination	32
4.6.1 Surface Sampling	32
4.6.2 Clean Room Diagnosis	32
5.0 Laboratory Test Results	35
5.1 Solvent Availability	35

5.2 Intentional Contamination: NVR Wipe Test	36
5.3 Contamination Test (ASTM E 1235)	38
5.3.1 Adventitious Contamination	38
5.3.2 Precontaminated Stainless Steel Witness Plates	39
6.0 Summary	45
6.1 NVR Solvent Replacement Recommendations	45
6.2 Technology Insertion	45
6.3 Further Test Needs	46
6.3.1 Wipers	46
6.3.2 Evaporation Techniques	46
6.3.3 Materials Compatibility	46
References	47
Appendix A: Hansen Parameters for Various Solvents	A-1
Appendix B: Specifications of Commercial Ethyl Acetate	B-1
B.1 Baxter (Burdick and Jackson)	B-1
B.2 Aldrich Chemical Company	B-2
Appendix C: Materials Safety Data Sheet for Ethyl Acetate	C-1

Figures

Figure 1. Total Hansen solubility parameter (MPa) ^½ for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.	8
Figure 2. Vector difference in Hansen solubility parameter (MPa) ^½ for various solvents, compared to dichloromethane.	9
Figure 3. Vector difference in Hansen solubility parameter (MPa) ^½ for various solvents, compared to 1,1,1 trichloroethane/ethanol mixture (NVR solvent).	10
Figure 4. Vapor pressure, in Torr, at 25°C for various solvents. The bold vertical bars indicate the practical working range for NVR analysis.	12
Figure 5. Overall screening score for various current and potential NVR solvents. See text for details.	17
Figure 6. Vector difference from NVR solvent blend for the solvents evaluated by Parks.	26
Figure 7. Vector difference from dichloromethane for the solvents evaluated by Parks.	27
Figure 8. Wipe test witness plate. Not shown to scale.	37
Figure 9. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with BOE Lube.	40
Figure 10. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with tetraphenyl dimethyl disiloxane.	41
Figure 11. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with squalane.	42
Figure 12. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with hexadecanol.	43
Figure A1. Hansen polarization force parameter (MPa) ^½ for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.	A-1
Figure A2. Hansen parameter for dispersion (MPa) ^½ for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.	A-2
Figure A3. Hansen parameter for hydrogen bonding (MPa) ^½ for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.	A-3

Tables

Table 1.	Flammability and Toxicity Hazard Assessment for Various Organic Compounds with Potential Application as NVR Solvents ^a	14
Table 2.	Summary of "Figures of Merit" for Solvent Properties, Toxicity, and Vapor Pressure.	16
Table 3.	Solvent Test Rankings from Martin Marietta CCAS Testing	20
Table 4.	Solvents Evaluated in Martin Marietta PJKS Test Program ^a	22
Table 5.	Rankings of NVR Solvent Candidates from LMSC Laboratory Tests.	23
Table 6.	Hansen parameter Analysis for Solvents Investigated by Parks: Differences from NVR Solvent Blend.	24
Table 7.	Hansen Parameter Analysis for Solvents Investigated by Parks: Differences from Dichloromethane.	25
Table 8.	Cleaning Efficiency Results from NASA MSFC Testing ^a	29
Table 9.	Immersion Test Results for 10 Solvents, Tested at 50°C	31
Table 10.	Classification of Product Cleanliness Levels	33
Table 11.	Solvent NVR Tests, 60 ml Samples, As-Received Solvents	35
Table 12.	Test Results for NVR Wipe of Test Samples Precontaminated with Squalane . . .	36
Table 13.	ASTM E 1235 Test Comparison Between Dichloromethane and Ethyl Acetate . .	38
Table 14.	Materials Used in ASTM E 1235-88 Tests	39

Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ACS	American Chemical Society
ASTM	American Society for Testing and Materials
B&J	Burdick and Jackson division of Baxter Corp.
CCP	Contamination Control Plan
CFC	Chlorofluorocarbon (also known under the trade name Freons®)
CFC-113	Trichlorotrifluoroethane
CGS	Centimeter-gram-second units of measure
CWA	Clean Work Area
CyHex	Cyclohexane
DCM	Dichloromethane, or methylene dichloride
DI	Deionized (water)
EGMBE	Ethylene glycol monobutyl ether (Butyl Cellosolve®)
EPA	Environmental Protection Agency
EtAc	Ethyl acetate
EtOH	Ethanol (ethyl alcohol)
ER	Eastern Range (formerly known as the Eastern Test Range, ETR)
HPLC	High Performance Liquid Chromatography
IPA	Isopropanol (2- propanol, isopropyl alcohol)
IUS	Inertial Upper Stage
LMSC	Lockheed Missiles and Space Co.
MIL STD	Military Standard
MSDS	Material Safety Data Sheet
MSFC	Marshall Space Flight Center
MTBE	Methyl tertiary butyl ether
NASA	National Aeronautics and Space Administration
NIOSH	National Institute of Occupational Safety and Health
NVR	Nonvolatile Residue (evaporation residue)
ODC	Ozone Depleting Chemical
ODS	Ozone Depleting Substance
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
PLF	Payload Fairing
PLFPF	Payload Fairing Processing Facility
PPM	Parts Per Million
SMC	U.S. Air Force Space and Missiles Systems Center
TCA	1,1,1 Trichloroethane
TCP	Tricresylphosphate
TLV	Threshold Limit Value
TOC	Total Organic Carbon
USAF	United States Air Force
WR	Western Range (formerly known as the Western Test Range, WTR)

1.0 Introduction

Control of contamination during processing and integration of spacecraft and launch vehicles is fundamental to insuring mission performance and longevity. Molecular contamination, or nonvolatile residue (NVR), is limited by selection of materials and the control of procedures and facilities.

Diagnosis of NVR accretion rates is accomplished using witness plates as described in ASTM E 1235-88 ["Standard Test Method for Gravimetric Determination of Non-volatile Residue (NVR) in Environmentally Controlled Areas for Spacecraft"].¹ A solvent wipe test documented in USAF Space Systems Division TR-89-63 ("Standard Method for Measurement of Non-volatile Residue on Surfaces") is used to assess hardware cleanliness.² These documents, or tailored versions, often define contractual requirements for US spacecraft and launch vehicle procurement and launch.^{3,4,5} These practices rely on the use of dichloromethane (methylene chloride), which is targeted for reduction under the EPA 33/50 program and the Clean Air Act, or a mixture of ethanol with 1,1,1 trichloroethane (methyl chloroform or TCA), which is a "Class 1" ozone depleting chemical.

This report documents work performed to select a non-ozone-depleting substitute for the two solvents used in the NVR diagnosis tests. A combination of solvent properties screening, literature review, and laboratory experimentation was used to select the recommended replacements. We conclude that ethyl acetate or ethyl acetate/cyclohexane azeotrope are the best candidates for replacing TCA and dichloromethane.

The second section of this report documents a review of Titan IV documentation to indicate the range of use of ODC's in Titan IV contamination control. The third section presents a screening of solvents for their inherent properties to guide selection of a "drop in" replacement solvent for NVR analysis. The fourth section of this report summarizes relevant research on this topic. The fifth section presents our laboratory results on the availability, purity, and effectiveness of the selected replacement. The sixth section presents a summary and indicates some additional work required for implementation of the recommended solvent substitution.

These NVR tests may involve the use of hazardous materials, operations, and equipment. The effort reported here does not purport to address all the safety problems associated with their use. It will be the responsibility of the user of any modified procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

2.0 Titan Program NVR Solvent Usage

Titan Program requirements for ODC solvent for contamination control needs were evaluated by reviewing the Contamination Control Plans for the Western Range³ and the Eastern Range.⁴ The WR contamination control plan for Space Launch Complex 4E is currently being re-written on account of a change in contractor responsibility⁶, but the needs for future operations will be similar to those in the past. The CCP's include mentions of fairing cleaning with chlorofluorocarbons. The recently installed ER carbon dioxide cleaning facility and the similar planned facility at the WR substantially obviate this need.

Though not detailed herein, processing documents for the Atlas launch vehicle similarly call for the use of the TCA/EtOH mixture in accordance with SD-TR-89-63.⁷

2.1 WR Contamination Control Plan

The WR CCP refers to ODC solvent usage as described below.

2.1.1 Referenced Documents

ML-C-813402C, "Cleaning Compound, Solvent, Trichlorotrifluoroethane" is referenced.

ASTM E 1235-88, "Standard Test Method for Gravimetric Determination of Non-Volatile Residue in Environmentally Controlled Areas for Spacecraft" is referenced. This test specifies methylene chloride, but tailored versions often use the TCA/Ethanol (EtOH) NVR solvent.

2.1.2 Payload Fairing Processing Facility/Clean Work Area (PLFPF/CWA)

The use of a CFC precision cleaning agent is mentioned. The list of approved materials for the PLFPF/CWA, table 5.2 of the reference document, which would identify other solvents is not provided in reference 3.

2.1.3 Clean Enclosure

The use of a CFC precision cleaning agent is mentioned. The list of approved materials, table 5.5 of the referenced document, lists trichloroethane.

2.1.4 Appendix C- Optional Services

This appendix calls out the procedure for nonvolatile residue wipe testing. The TCA/EtOH NVR solvent is specifically required.

2.1.5 Appendix D- Titan IV Payload Fairing Contamination Control Plan

Final in-factory cleaning requires use of an unidentified solvent called "STM0752." Air conditioning ducts are to be rinsed with TCA and then vapor degreased with an unspecified solvent. The inner surfaces of the fairing are to be flushed with chlorofluorocarbon 113 (MIL-C-81302, Type I).

2.2 ER Contamination Control Plan

The ER CCP refers to ODC solvent usage as described below.

2.2.1 Referenced Documents

ML-C-813402C, "Cleaning Compound, Solvent, Trichlorotrifluoroethane" is referenced.

2.2.2 Payload Fairing Processing

Spray cleaning with trichlorotrifluoroethane is required.

2.2.3 Appendix C- Additional Services

An NVR test procedure similar to ASTM E 1235-88 is described which requires the TCA/EtOH NVR solvent. This appendix calls out the procedure for nonvolatile residue wipe testing. The TCA/EtOH NVR solvent is specifically required.

2.2.4 Upper Stage Contamination Control Plans

Centaur and IUS contamination control plans are provided as appendices to reference 4. They call out uses of TCA, TCA/EtOH, and trichlorotrifluoroethane similar to those in the main contamination control plan.

3.0 Solvent Screening

This section describes a literature-based screening of candidate "drop in" replacement solvents for the two NVR tests. To insure a well understood heritage to existing practice, materials' solvent properties, vapor pressure, cleanliness and stability, safety and health issues, and environmental issues were evaluated.

Some general guidelines were followed in selecting the initial set of solvents for screening. Materials that are class 1 ozone depleting chemicals were not considered as viable replacements for methylene chloride and TCA, for obvious reasons. Only pure materials, not commercial mixtures were considered. Aside from a philosophical desire not to endorse one vendor's mixture over another, relying on a proprietary mixture (which may be subject to unannounced changes in formulation) is undesirable in a standard practice.

These two NVR tests were designed originally to provide a method for comparing facilities and ascertaining facility cleanliness trends, but not necessarily to provide an absolute quantitative determination of a specific type of NVR.⁸ Therefore, it is important to remember that the goal of finding a replacement solvent for these standard tests is not necessarily to find the "best" solvent for a specific type of nonvolatile residue. Rather, the goal is to find those replacement solvents which most closely match the solvent properties of methylene chloride and the NVR mixture. Initial screening of commonly available organic solvents relies on the "Hansen parameters" characterization of solvents.⁹ These parameters provide a quantitative representation of the "like dissolves like" rule of thumb so familiar to chemists.

Candidate solvents must have vapor pressures similar to dichloromethane or the TCA/EtOH mixture. If the vapor pressure is too high, the test cannot be completed under standard laboratory conditions. If the vapor pressure is too low, the evaporation process for the gravimetric analysis will take too long, which would result in an unacceptable turnaround rate and risk contamination of the test sample. In the extreme case, the vapor pressure of the solvent may become comparable to the vapor pressure of the "nonvolatile" residue being diagnosed. The NVR tests, as modified, may involve the use of hazardous materials, operations, and equipment. Candidate solvents are screened on the basis of 8 hour threshold limit values, compared with their room temperature vapor pressures.

The overall results of candidate solvent screening are captured in a semiquantitative selection matrix. Two promising candidates for replacement solvents emerge from this screening: ethyl acetate and methyl acetate.

3.1 Solvent Properties Screening

In selecting a solvent for any particular application, chemists generally rely on the rule of thumb that "like dissolves like." For example, a non-polar solute, such as a saturated hydrocarbon, is generally best dissolved by a non-polar solvent, such as heptane. Therefore, in selecting replacements for dichloromethane and the NVR solvent blend, one looks for a solvent that is as much "like" them as possible.

One quantitative approach to "likeness" is to use "solubility parameters" to describe the solvents.⁹ One of the simplest of these parameters, the Hildebrand parameter, is related to the cohesive energy density (cohesive energy per unit volume). The cohesive energy is the energy associated with the net attractive interactions of a material (as compared to an ideal vapor at the same temperature). The cohesive energy density, c , is given by

$$c = -\frac{U}{V} \quad (1)$$

where U is the total molar cohesive energy and V is the molar volume. The units of c are the same as pressure. The Hildebrand parameter, δ , is defined as

$$\delta = c^{1/2} \quad (2)$$

Barton explains the rationale for quantifying solubility in terms of molecular cohesion, as follows.

A material with a high δ value requires more energy for dispersal than is gained by mixing it with a material of low cohesion parameter, so immiscibility results. On the other hand, two materials with similar δ values gain sufficient energy on mutual dispersion to permit mixing.

A refinement of the Hildebrand parameter consists of the three-component Hansen parameters. Hansen proposed dividing the total cohesive energy into terms corresponding to dispersion forces, polar forces, and hydrogen bonding, as shown in Eq. (3).

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

The total Hansen parameter, δ_t , is equivalent to the Hildebrand parameter. In applying the Hansen parameters, one should remember that they do not take into account any specific chemical or ionic interactions. Indeed, the approach is intended to provide an estimate of the properties of mixtures considering only the properties of the individual components. Barton⁹ has provided extensive tables of Hansen parameters for a wide variety of organic chemicals. Figure 1 presents the total parameter as a bar graph, for a variety of organic solvents. Indications of the range of these parameters spanned by 1,1,1 trichloroethane and dichloromethane are provided.

The Hansen parameters are used here to identify likely candidate replacement solvents.* The most compact comparison is provided by considering the magnitude of the vector (in Hansen parameter space) from methylene chloride or NVR solvent to the candidate solvent. The length of the vector from methylene chloride (DCM) to solvent i is given by

$$d_i^{DCM} = [(\delta_{d_{DCM}} - \delta_{d_i})^2 + (\delta_{p_{DCM}} - \delta_{p_i})^2 + (\delta_{h_{DCM}} - \delta_{h_i})^2]^{1/2} \quad (4)$$

with the distance to NVR solvent defined analogously. Figures 2 and 3 present bar graphs of the vector differences between the various solvents considered and dichloromethane and NVR solvent blend. The best matches appear to be methyl isobutyl ketone, methyl ethyl ketone, n-butyl acetate, methyl acetate, ethyl acetate, and tetrahydrofuran.

* The Hansen parameters for NVR solvent were estimated using the volume weighted average of the parameters for 1,1,1 trichloroethane and ethanol.

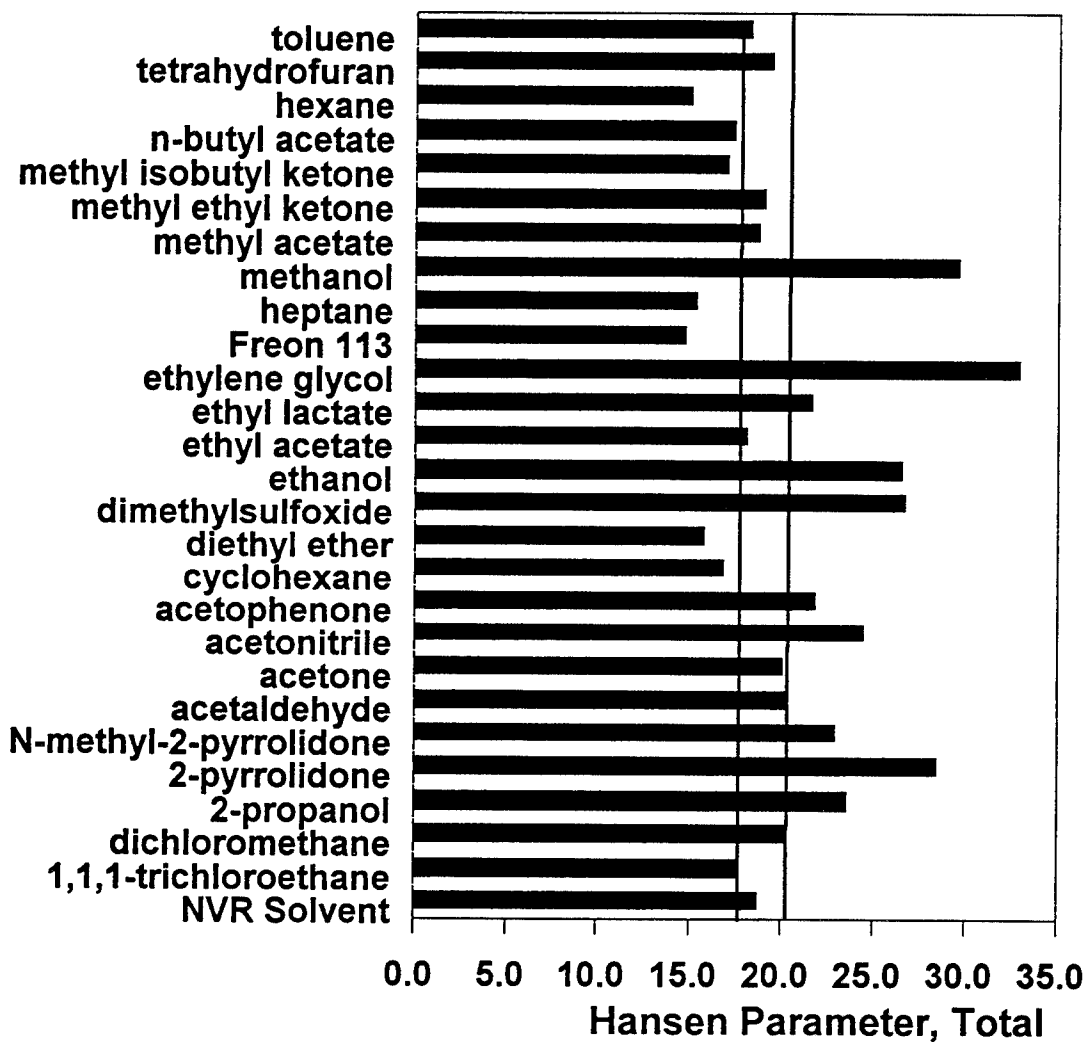


Figure 1. Total Hansen solubility parameter (MPa)^{1/2} for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.

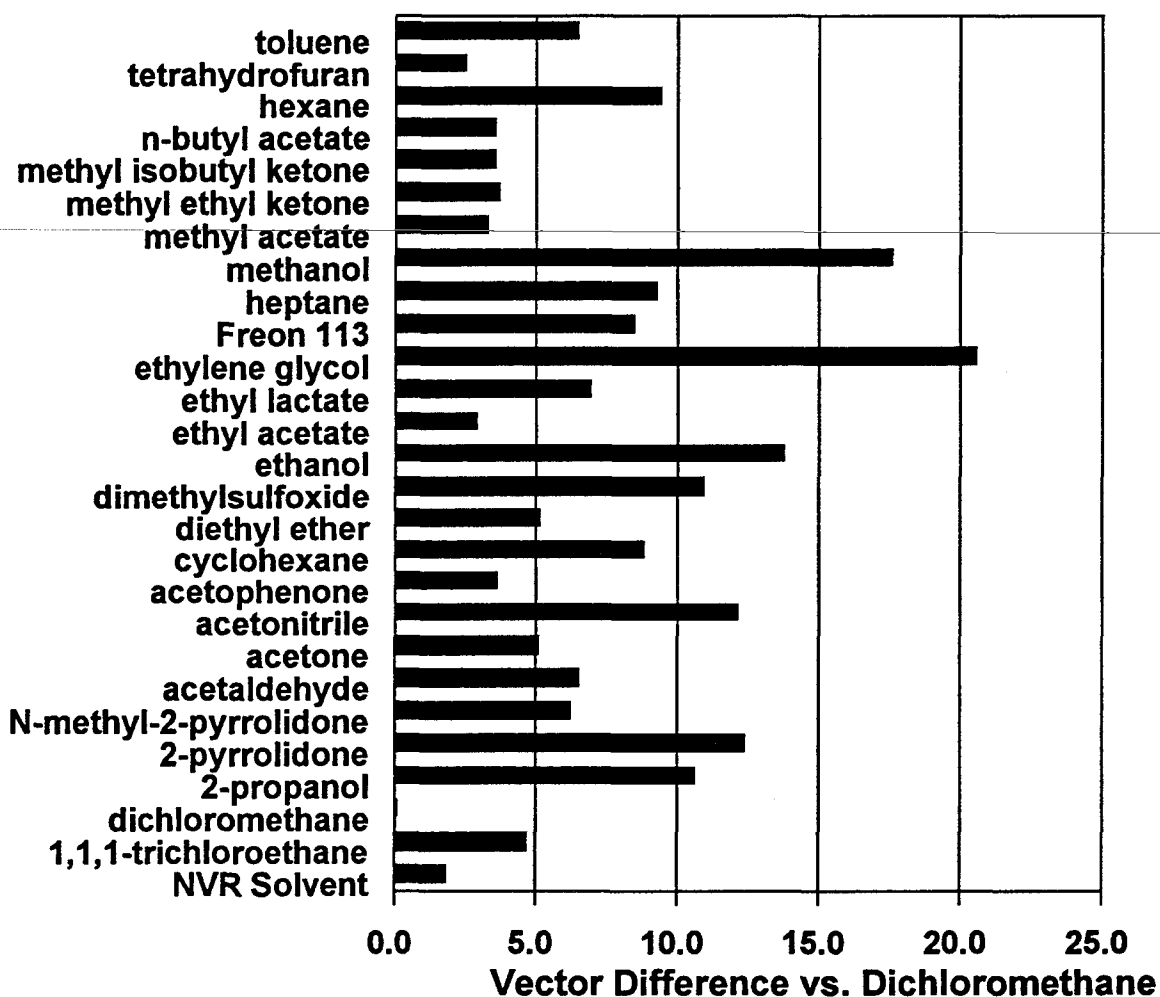


Figure 2. Vector difference in Hansen solubility parameter (MPa)^{1/2} for various solvents, compared to dichloromethane.

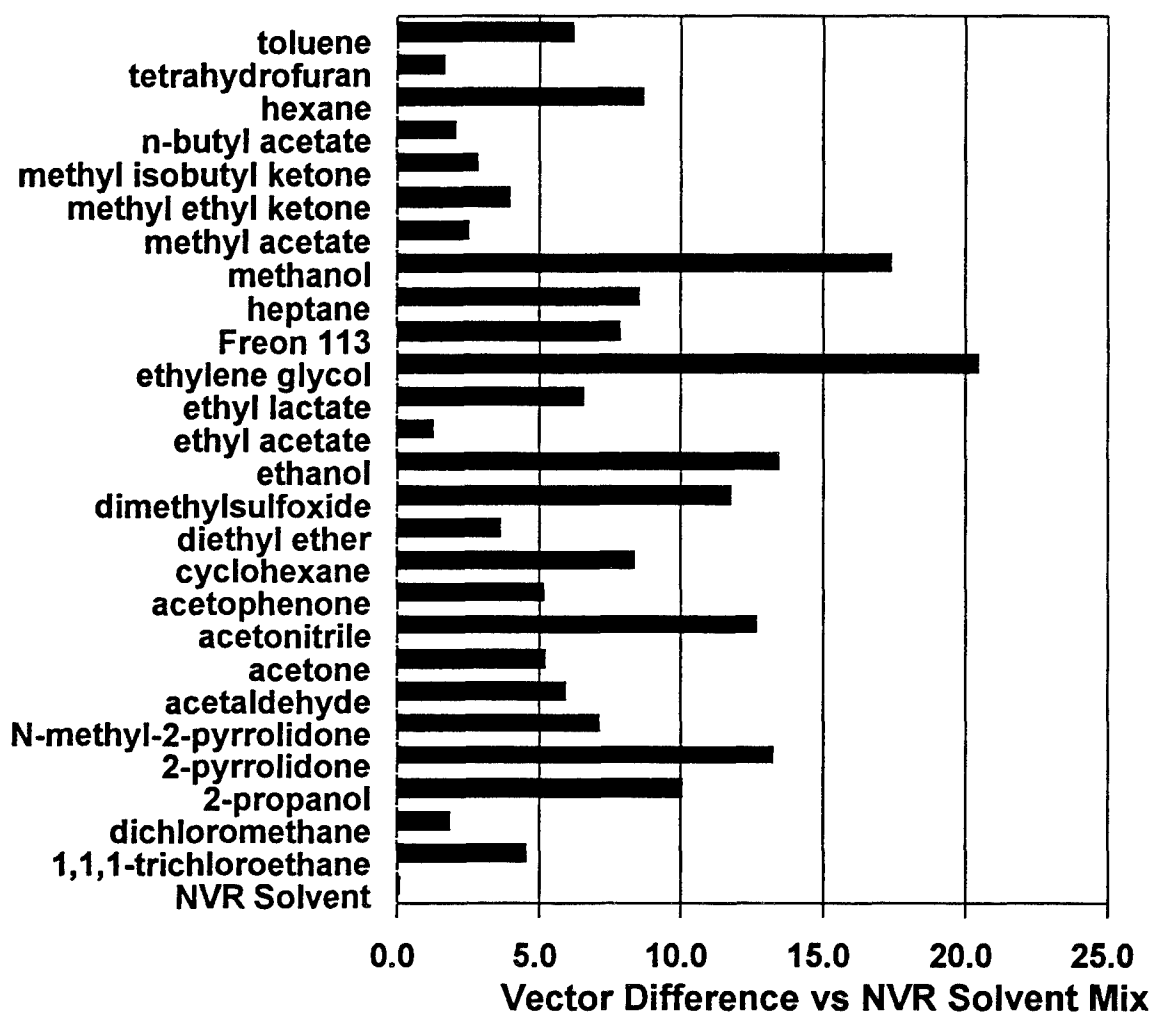


Figure 3. Vector difference in Hansen solubility parameter $(\text{MPa})^{1/2}$ for various solvents, compared to 1,1,1 trichloroethane/ethanol mixture (NVR solvent).

3.2 Vapor Pressure Analysis

A solvent used for nonvolatile residue analyses needs to have an appropriate vapor pressure near room temperature. The vapor pressure cannot be so high that the solvent is difficult to handle (evaporates too rapidly) during rinsing of witness plates or wiping hardware under test. Conversely, the vapor pressure must not be so low that the near-room-temperature evaporation used in the gravimetric analyses takes an excessively long time.* Vapor pressure data were obtained from standard reference works.^{10,11,12} In most cases, these data took the form of discrete values of vapor pressure vs. temperature. These data were fit to an Arrhenius function. The figure of merit used to compare solvents is their vapor pressure at 25°C. Figure 4 presents a bar chart of this figure of merit. The two vertical lines indicate the range of useful vapor pressures, as determined from experience. Diethyl ether is about as volatile a material as one would want to handle in the NVR tests. Isopropyl alcohol is about as nonvolatile as would be desirable.

This sorting of the solvents considered suggests that diethyl ether, acetone, methyl acetate, tetrahydrofuran, hexane, methanol, methyl ethyl ketone, cyclohexane, acetonitrile, ethyl acetate, ethanol, heptane, and isopropanol are viable candidates for replacing dichloromethane and the NVR mix.

* Note that this requirement for a moderate vapor pressure differs from what one would wish in a cleaning solvent used to wash parts (e.g., in an ultrasonic cleaner). In that case, low vapor pressure (evaporation rate) is a virtue.

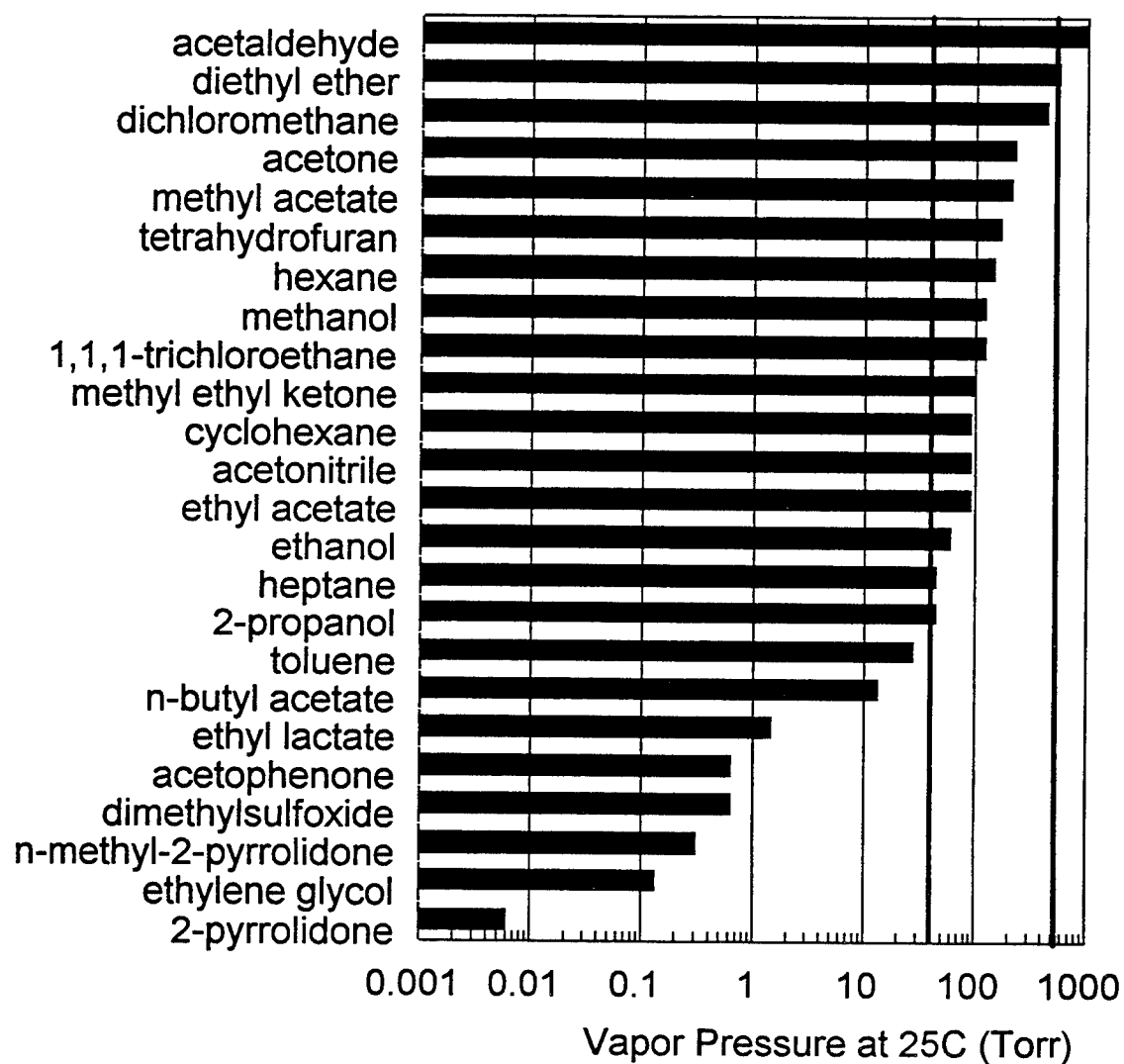


Figure 4. Vapor pressure, in Torr, at 25°C for various solvents. The bold vertical bars indicate the practical working range for NVR analysis.

3.3 Hazard Evaluation

Handling organic solvents presents both toxicity and flammability hazards. Almost all conceivable substitutes for the chlorocarbon and chlorofluorocarbons used in NVR analysis present one or both of these hazards. For the purpose of this screening, four figures of merit were examined: (1) the "Threshold Limit Value" for exposure to the material; (2) an inhalation hazard ratio⁶ (IHR, defined as the ratio of the saturated vapor concentration at 25°C to the TLV); (3) "Immediately Dangerous to Life or Health" (IDLH) concentrations; and (4) the "Flash Point."

The TLV data are generally the OSHA permissible exposure limits. These are the concentrations that must not be exceeded during any 8 hour work shift of a 40 hour work week.¹³

The IDLH values "represent the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without a respirator and without experiencing any escape-impairing (e.g. severe eye irritation) or irreversible health effects."¹³

The inhalation hazard ratio gives a feeling for the degree of ventilation required for handling the material in question.

Since virtually all the credible short-term replacements for ODC's in the NVR tests are volatile and flammable, the flash point data are not given significant weight in screening potential solvents. In addition to this practical consideration, the facts that these tests are performed in controlled, laboratory-like environments, by trained personnel, using small quantities of solvent mitigates the concern over solvent flammability.

Threshold limit value, IDLH, and flash point data were taken from standard literature sources.^{13,14,15} Table 1 presents the data. TLV's, IDLH's, and IHR's with zero values indicate that no data were available for those materials (ethyl lactate, dimethylsulfoxide, and the pyrrolidones). All of the materials examined for which the TLV data are available show a lower IHR and higher TLV than dichloromethane. However, several are more hazardous, by both measures, than 1,1,1 trichloroethane, the more hazardous part of NVR solvent. Table 1 indicates other hazard information. Some of the materials are class 1 ODC's. Several are on the EPA 17 list. Dimethylsulfoxide is an efficient skin penetrant, making it particularly dangerous when contaminated with other potentially toxic materials. Dichloromethane is a suspected carcinogen. Like most ethers, tetrahydrofuran can decompose into explosive peroxides.

Table 1. Flammability and Toxicity Hazard Assessment for Various Organic Compounds with Potential Application as NVR Solvents^a

Solvent	Flash Point	TLV ppm	Inhalation Ratio	IDLH (ppm)	Comments
1,1,1-trichloroethane	none	350	451	1000	Class 1 ODC
2-propanol	12	400	140	12000	
2-pyrrolidone	110				no TLV data
acetone	-19	750	386	20000	
acetonitrile	6	40	2888	4000	
cyclohexane	-18	300	396	1000	
dichloromethane	none	50	11184	5000	carcinogen, EPA 17
diethyl ether	-45	400	1806	19000	
dimethylsulfoxide	88				skin penetrant, no TLV
ethanol	12	1000	74		
ethyl acetate	-4	400	288	10000	
ethyl lactate ¹¹	49				no TLV data
ethylene glycol	111	50	3		
CFC-113	48	1000	434	4500	Class 1 ODC
heptane	-4	400	141	5000	
hexane	-22	50	3816	5000	
methanol	11	200	796	25000	
methyl acetate	-16	200	1375	10000	
methyl ethyl ketone	-6	200	630	3000	EPA 17
n-butyl acetate	22	150	112	10000	
n-methyl-2-pyrrolidone	86				no TLV data
tetrahydrofuran	-14	200	1086	20000	explosion hazard in distillation
toluene	4	50	703	2000	EPA 17

^a blank values indicate no data were located.

3.4 Screening Summary

The previous three subsections of this report have presented screening data for assessing the likely utility of various organic solvents as replacements for dichloromethane and the 1,1,1 trichloroethane/ethanol solvent mixture in nonvolatile residue tests. In this subsection a semiquantitative combination of those screening data is presented, and candidate replacement solvents are identified. The rating scales were designed to give heaviest weighting to the solvent properties, as described by the Hansen parameters. Roughly equal weighting was given to vapor pressure and toxicity.

To put the Hansen parameter analysis on a roughly "one to ten scale," the following figures of merit for solvent i were calculated [see Eq. (4)].

$$\text{Hansen DCM} = \frac{(20 - d_i^{\text{DCM}})}{2} \quad (5)$$

A quantity *Hansen NVR* is defined analogously.

Table 1 shows that virtually all of the solvents under consideration require some degree of ventilation. Therefore, the TLV, not the IHR was used as a rating parameter. To put the data on a 1-10 scale the TLV in volume ppm was divided by 100. If a candidate solvent is on the EPA 17 list, the toxicity rating was arbitrarily assigned a value of -5. Materials for which no TLV data were available received a zero score in this category. A fairly insensitive rating scale for vapor pressure was chosen, the logarithm to base 10 of the 25°C vapor pressure of the material, in Torr. This provided a scale spanning roughly -3 to +3.

The individual rating data (rounded to integer values) are presented in Table 2. The total ratings are shown in Figure 5. The chosen scale provided benchmark values for NVR solvent and dichloromethane of about 25. Five potential solvent replacements rated above 20 on this scale: acetone, diethyl ether, ethyl acetate, methyl acetate, and tetrahydrofuran.

The hazard properties of the two ethers (diethyl ether and tetrahydrofuran) militate against their use in NVR testing. Diethyl ether is at the extreme high end of the range of useful volatility, and presents a severe fire and explosion hazard. Tetrahydrofuran, a cyclic ether, shares a property common to many ethers: it can decompose to form explosive peroxides. "Inhibited" materials are available, but this involves contamination, for example, with 250 ppm of butylated hydroxytoluene, which is a solid with a 69°C melting point.¹⁶

In the overall rating, acetone scored among the top candidates. This rating is somewhat misleading in that acetone scored high in the toxicity benchmark, but lower in the solubility benchmarks. Furthermore, it is substantially more polar than the solvents for which replacements are sought. Testing has shown that acetone is not as effective for some contaminants as other solvents (see below). However, it has some advantages. It is readily available at many laboratories. Indeed, it is already an approved material for use at many U.S. launch sites.

Table 2. Summary of "Figures of Merit" for Solvent Properties, Toxicity, and Vapor Pressure

Solvent	Hansen DCM	Hansen NVR	Toxicity	Vapor Pressure	Total
NVR Solvent ^a	9	10	4	2	25
1,1,1-trichloroethane	8	8	4	2	22
dichloromethane	10	9	4	3	26
2-propanol	5	5	4	2	15
2-pyrrolidone	4	3		-2	5
n-methyl-2-pyrrolidone	7	6		-1	13
acetone	8	7	8	2	25
acetonitrile	4	4	0	2	10
cyclohexane	6	6	3	2	16
diethyl ether	7	8	4	3	22
dimethylsulfoxide	5	4		0	8
ethanol	3	3	10	2	18
ethyl acetate	9	9	4	2	24
ethyl lactate	7	7		0	13
ethylene glycol	0	0	1	-1	-1
heptane	5	6	4	2	17
methanol	1	1	2	2	7
methyl acetate	8	9	2	2	21
methyl ethyl ketone	8	8	-5	2	13
n-butyl acetate	8	9	2	1	20
hexane	5	6	1	2	14
tetrahydrofuran	9	9	2	2	22
toluene	7	7	-5	1	10

^a Assuming 1,1,1 trichloroethane vapor pressure.

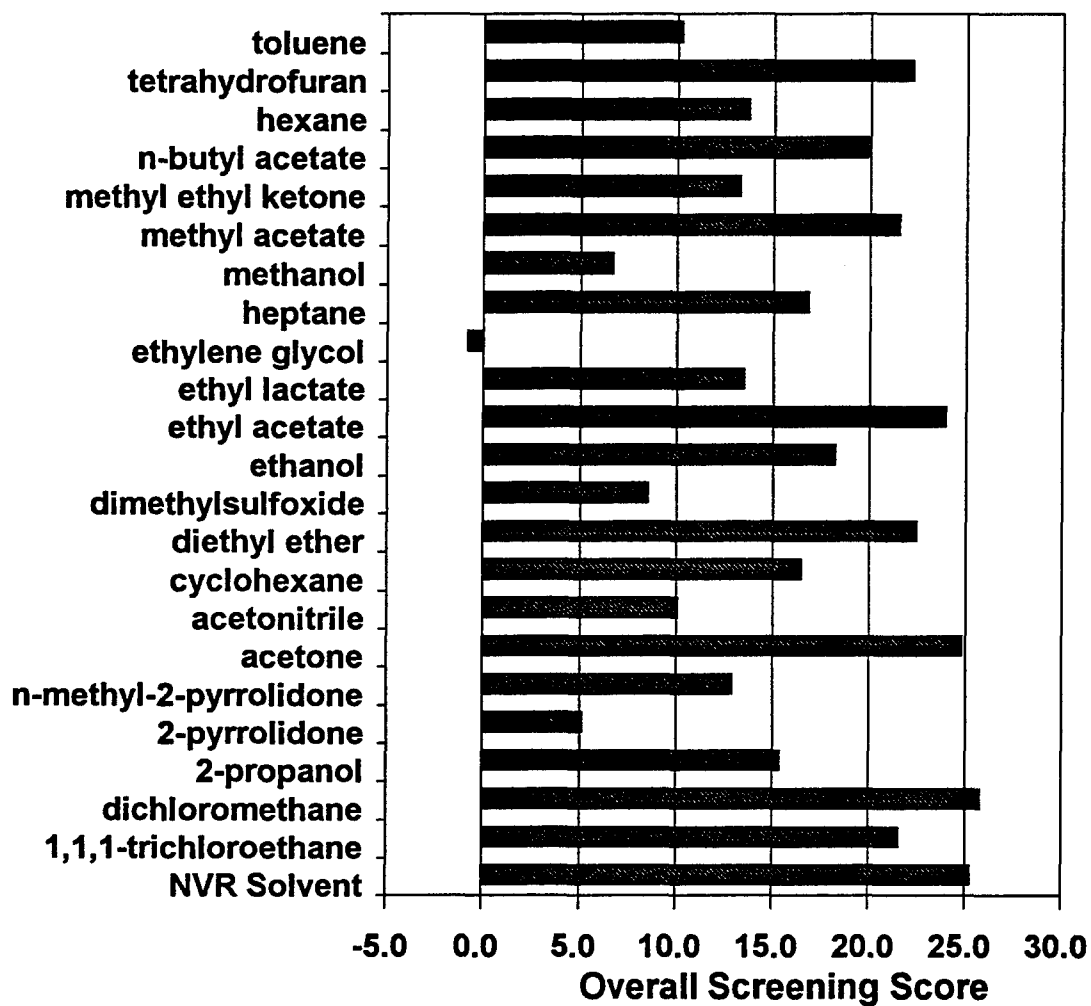


Figure 5. Overall screening score for various current and potential NVR solvents. See text for details.

4.0 Review of Relevant Testing Results

The concern over replacement of ODC solvents is widespread. Currently large portions of the trade journals Microcontamination and Precision Cleaning are devoted to non-ODC cleaning technology reports and advertisements. Substantial efforts have been reported that evaluate commercial aqueous and non-aqueous cleaners as replacements for CFC's and TCA.^{17,18,19,20} Strategies and "expert systems" have been proposed for how to select the best substitute for an ODC cleaning solvent.^{21,22} Clearly, a review of this entire area is beyond the scope of this project. Indeed, much of the work in this field is not relevant to the problem at hand, because the characteristics of a good cleaner do not match completely the characteristics of a good solvent for gravimetric NVR analysis (see above, Section 3.0).

There is, however, a body of work relevant to the NVR solvent replacement problem. This section of this report summarizes some of the work performed at other laboratories that is particularly relevant to the Titan IV and Atlas NVR solvent replacement issue.

4.1 Martin Marietta CCAS Testing

Barrows has reported the results of "qualitative visual inspection laboratory test[s]" to screen potential replacements for the NVR solvent blend.²³ Oils used in the manufacture and processing of the Titan IV payload fairing were coated onto glass plates, and the ability of various solvents to remove the oils were evaluated visually. The solvents were rated on a 1-5 scale, for their absolute effectiveness in removing the contaminant and a 1-4 scale in relative effectiveness. (The tests involved comparison of solvents in groups of four.) The contaminants tested were "Boe Lube," "Amber Tap," "Rustlic Oil," and "WD-40."

To compare the solvents, Barrows calculated a "summed rank," which is the sum over the four contaminants tested of the product of the absolute visible rating (1-5) and the relative rating (1-4), for the five sets of tests performed. Table 3 presents the results of this ranking.

The mixtures Barrows evaluated were not azeotropes. They were 50:50 blends. However, minimum boiling azeotropes exist for acetone/hexane (59/41), ethanol/hexane (21/79), and ethanol/toluene (68/32).²⁴ There are good reasons to favor azeotropes over blends, if mixed solvents are to be considered for any particular NVR or precision cleaning application (see below, Section 4.3).

Note that Table 3 shows that ethyl acetate is quite effective compared to other pure solvents evaluated, and is competitive with the mixtures.

Barrows has indicated that, in other testing, hexane performed quite well for NVR evaluation.²⁵ The toxicity of this material militates strongly against using it as a routine NVR solvent, in work environments where it cannot be contained within an exhausted fume hood.

Table 3. Solvent Test Rankings from Martin Marietta CCAS Testing

Test #	Solvent	Summed Rank
1	isopropanol/water	4
	isopropanol	4
	acetone	61
	hexane	47
2	toluene	55
	tbme ^a	7
	ethanol	35
	acetone/hexane ^b	45
3	hexane/ethanol ^b	13
	toluene/ethanol ^b	45
	acetone/hexane ^b	43
	ethyl acetate	50
4	hexane/toluene ^b	22
	acetone/toluene ^b	51
	ethyl acetate/toluene ^b	31
	ethyl acetate/acetone ^b	33
5	acetone/toluene ^b	59
	ethanol/toluene ^b	32
	ethyl acetate	45
	acetone	20

^a Presumed to be methyl tertiarybutyl ether

^b All mixtures were 50:50 blends.

4.2 Martin Marietta PJKS Testing

King and Giordano have reported a series of tests performed to identify a replacement for CFC-113 in NVR testing at the Martin Marietta PJKS facility.^{26,27} Table 4 lists the solvents evaluated in the Martin Marietta work and the surface contaminants used in their evaluation. The test contaminants they used were Mobil EP2 (hydrocarbon), Drilube 822 (silicone), MIL-6083 Hydraulic oil, Dykem layout fluid, and Krytox 240ac (fluorocarbon).

The top performers in their initial coupon test screening were methyl-tertbutyl ether, tetrahydrofuran, ethyl acetate, and acetone. Six of the solvents were used in more detailed tests involving cleaning and validation of fittings. The numbers in Table 4 indicate the ranking of the solvents in the detailed tests.

King and Giordano concluded that "ethyl acetate performs as well as CFC-113 in removing both contaminants from fittings." They recommended ethyl acetate over the two ethers that performed better because of the chemical instability of the ether solvents. (See above.)

They also noted that the Krytox fluorinated grease was removed only by CFC-113 and by Tribolube 197 (a perfluorinated compound). This is an important point to remember. There are some special classes of NVR, such as perfluorinated lubricants and greases, that are not amenable to analysis by a "generic" NVR solvent. For processes or facilities where such materials are used, a specific cleanliness validation test needs to be devised, or the standard tests tailored to use an effective solvent.

King and Giordano also noted that no reactions were apparent when ethyl acetate was mixed with nitrogen tetroxide or Aerozine 50 (a 50-50 blend of hydrazine and unsymmetrical dimethyl hydrazine).

Compatibility tests performed at Martin indicated that ethyl acetate damaged "Plexiglass." O-rings made from Teflon®, butyl rubber, and Viton® all showed some weight gain after 72 hours immersion in ethyl acetate, but showed "no visible degradation."

Table 4. Solvents Evaluated in Martin Marietta PJKS Test Program^a

Rank	Solvent
1	methyl tertbutyl ether
2	tetrahydrofuran
3	CFC-113
4	ethyl acetate
5	acetone
6	hexane
7	ethanol
	tribolube 197
	cyclohexane
	toluene
	trichloroethane
	perchloroethylene
	methylene chloride
	methyl ethyl ketone
	methyl acetate
	butoxyethanol
	n methyl pyrrolidone
	isopropanol
	purified water (two types)

^a Rankings are intercomparison of the seven numbered solvents only.

4.3 Lockheed Missiles and Space Corporation Testing

4.3.1 Summary of Results

Andreas Parks at Lockheed Missiles and Space Corporation, in Sunnyvale CA, has described a series of tests of various candidate replacement solvents.²⁸ Table 5 presents his quantitative ranking of solvents for their ability to remove a variety of residues. The top rated solvent, a cyclohexane/ethyl acetate azeotrope, is effective for all of the materials tested except water-based lubricants.

The azeotropes that Parks identified as being good replacement solvents have much to recommend them. The cyclohexane/ethyl acetate mixture was very good at removing a variety of contaminants. The mixture is a true azeotrope (as are all the cyclohexane mixtures Parks tested).²⁴ This means that the solvent mixture can be purified (or re-purified) in a single distillation step, rather than purifying two separate solvents, and blending them. Cyclohexane does not have as severe toxicity concerns as hexane.

4.3.2 Hansen Parameter Evaluation of LMSC Solvents

Table 6 and Table 7 present a Hansen parameter evaluation of the solvents considered by Parks. Figure 6 and Figure 7 indicate that the vector differences from NVR solvent blend and DCM are not as small as ethyl acetate's.

The detailed ratings of solvents in any particular set of tests depend on the solutes chosen for evaluation. However, one possible explanation of the good performance of the azeotropes compared to pure ethyl acetate can be surmised from the details of this Hansen parameter analysis. The azeotropes of cyclohexane provide a better match with the dispersion energies of the two halogenated solvents, and these dispersion forces are the strongest of the three for the halogenated solvents.*

Table 5. Rankings of NVR Solvent Candidates from LMSC Laboratory Tests

Ranking	Solvent	Comment
1	cyclohexane/ethyl acetate	azeotrope 44:56
2	dichloromethane	
3	TCA/ethanol	NVR solvent blend
4	CFC-113	
5	cyclohexane/ethanol	azeotrope
6	ethyl acetate	
7	cyclohexane/isopropanol	azeotrope
8	hexane	
9	methyl-tertbutyl ether	
10	perchloroethylene	
11	isopropanol	

* Also known as London or Van der Waals forces, the dispersion forces which arise from the polarizability of molecules often dominate the long-range attractions between molecules.

Table 6. Hansen parameter Analysis for Solvents Investigated by Parks: Differences from NVR Solvent Blend

Solvent	Molar Volume (cgs)	Hansen Parameters (differences from NVR solvent)				
		Dispersion	Polarization	Hydrogen Bonding	Total	Vector
1,1,1-trichloroethane	15.2	0.3	-1.1	-4.3	-1.0	4.5
CyHex/EtAc	18.0	-0.4	-2.6	-2.6	-1.7	3.7
dichloromethane	-21.3	1.5	0.9	-0.3	1.6	1.8
NVR Solvent	0.0	0.0	0.0	0.0	0.0	0.0
CFC-113	34.0	-2.0	-3.8	-6.4	-4.0	7.7
CyHex/EtOH	1.9	-0.2	-2.9	-0.7	-1.0	3.0
ethyl acetate	13.3	-0.9	-0.1	0.8	-0.6	1.2
CyHex/IPA	10.9	-0.2	-3.5	-1.1	-1.3	3.7
hexane	46.4	-1.8	-5.4	-6.4	-3.8	8.6
mtbe						
perchloroethylene	15.9	2.3	1.1	-3.5	1.6	4.3
2-propanol	-8.4	-0.9	0.7	10.0	4.8	10.0

Table 7. Hansen Parameter Analysis for Solvents Investigated by Parks: Differences from Dichloromethane

Solvent	Molar Volume (cgs)	Hansen Parameters (differences from DCM)				
		Dispersion	Polarization	Hydrogen Bonding	Total	Vector
1,1,1-trichloroethane	36.5	-1.2	-2.0	-4.0	-2.6	4.6
CyHex/EtAc	39.2	-1.9	-3.5	-2.2	-3.3	4.6
dichloromethane	0.0	0.0	0.0	0.0	0.0	0.0
NVR Solvent	21.3	-1.5	-0.9	0.3	-1.6	1.8
CFC-113	55.3	-3.5	-4.7	-6.1	-5.6	8.5
CyHex/EtOH	23.2	-1.7	-3.8	-0.3	-2.6	4.1
ethyl acetate	34.6	-2.4	-1.0	1.1	-2.2	2.8
CyHex/IPA	32.1	-1.7	-4.4	-0.7	-2.9	4.7
hexane	67.7	-3.3	-6.3	-6.1	-5.4	9.4
mtbe	-63.9					
perchloroethylene	37.2	0.8	0.2	-3.2	0.0	3.3
2-propanol	12.9	-2.4	-0.2	10.3	3.2	10.6

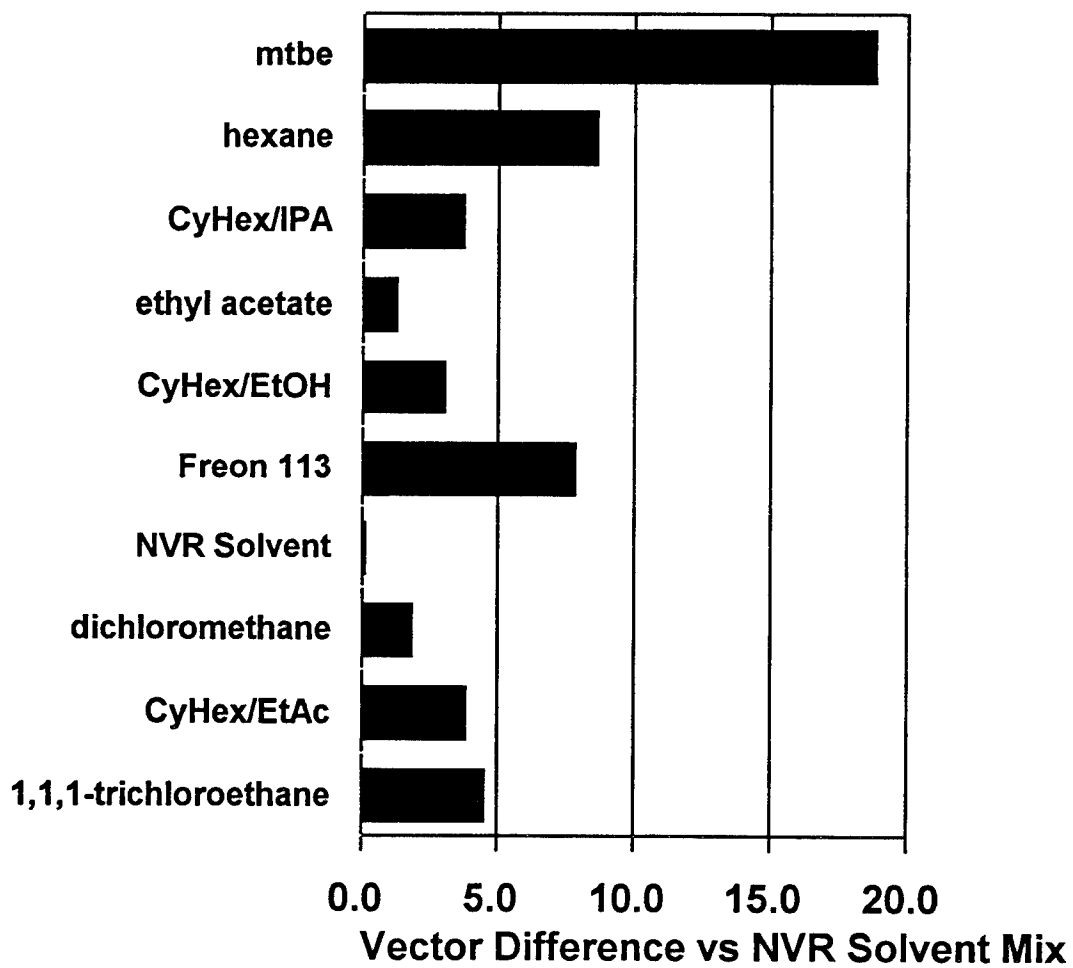


Figure 6. Vector difference from NVR solvent blend for the solvents evaluated by Parks.

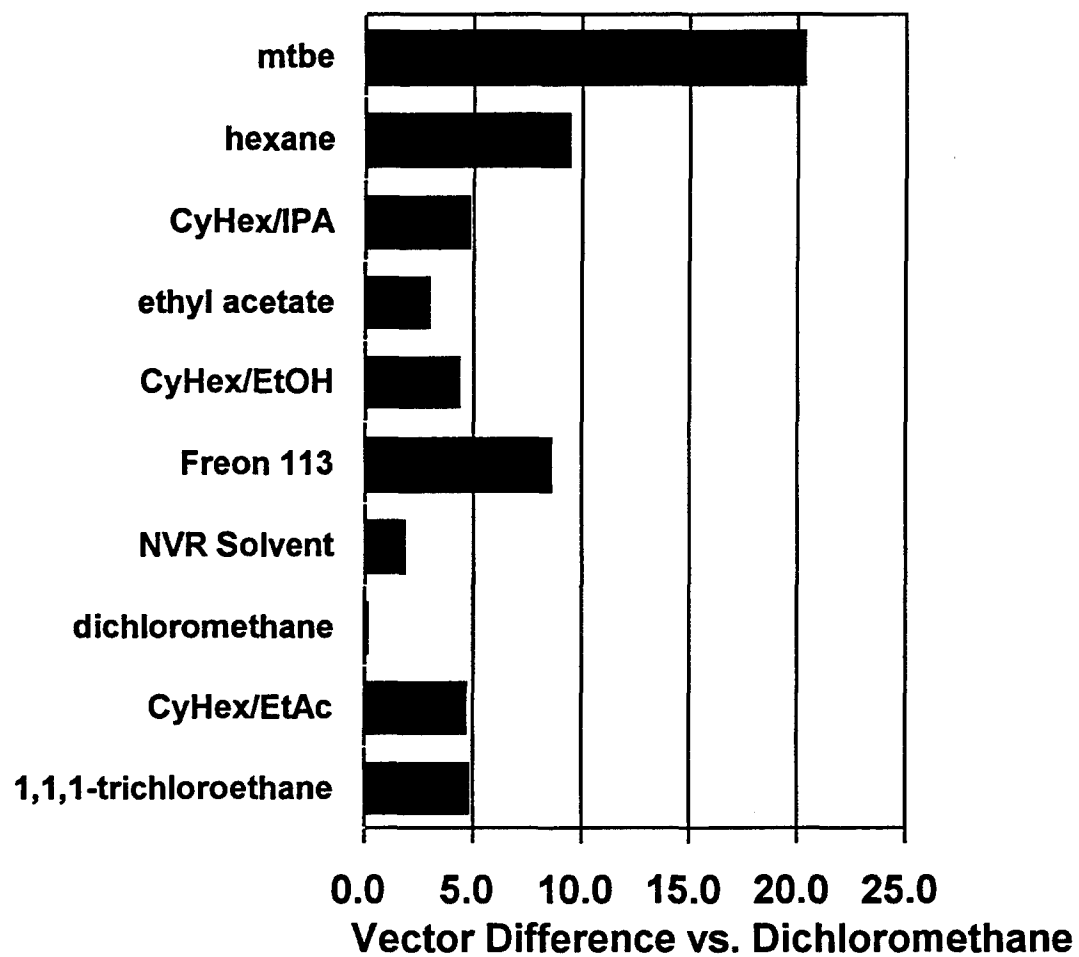


Figure 7. Vector difference from dichloromethane for the solvents evaluated by Parks.

4.3.3 Comments on the Use of Cyclohexane/Ethyl Acetate Azeotrope

As discussed above, the azeotropes identified by Parks have much to recommend them for generic NVR analysis. Both experiment and theory indicate their utility. The vapor pressures of the component are in the acceptable range, and the TLV of cyclohexane, 300 ppm, is in the acceptable range.

We see only one significant disadvantage to the use of this solvent for NVR analysis. So far, we have not identified a commercial vendor for the material. Parks blended and purified his own solvents, and for large laboratories, that may be an economically viable option.

However, in the past, users of these NVR tests have sought to procure rather than produce the test solvents. One should note that even before the ozone-depleting nature of the NVR solvent blend became a concern, it was becoming difficult to procure because the laboratories that purified the mixture were leaving the market for business reasons.²⁹

4.4 NASA Marshall Space Flight Center Testing

NASA MSFC has reported testing of alternative solvents for NVR determination as a part of their CFC Replacement Critical Area Response.³⁰

Ross reports³⁰ gravimetric testing of the cleaning efficiency of several solvents for Krytox oil, a silicon oil, a mineral oil, a hydraulic oil, a halocarbon grease, a Dow Corning silicon vacuum grease, and "phosphate ester TCP."^{*} The procedure followed was to deposit 1, 5, and 10 mg of each contaminant on separate aluminum weighing pans. The pans were rinsed with 100 ml of solvent and allowed to dry, and their weight was recorded to ascertain the amount of contaminant remaining.^{**}

Table 8 indicates the solvents tested, and the percent removal (cleaning efficiency) for the seven contaminant types. The Krytox oil used was not specified. The high efficiencies of all of the solvents in removing this material are surprising, compared to the poor performance of all but CFC's and perfluorocarbons in removing Krytox grease in the PJKS testing.

Ross concludes that an "85:15 mixture of IPA and EGMBE [ethylene glycol monobutyl ether]

Table 8. Cleaning Efficiency Results from NASA MSFC Testing^a

Solvent	Mineral Oil	Hydraulic Oil	Krytox Oil	Silicone Oil	Vacuum Grease	Halo-carbon Grease	TCP
DI Water (70°C)	33	58	78	97	0	58	32
isopropanol	95	98	100	100	35	95	96
semiaqueous ^b	8	8	91	88	2	64	66
Cellosolve/IPAc ^c	100	100	99	99	100	91	99
Vertrel 245 ^d	15	11	98	96	3	92	5
PF 5060 ^e	13	6	100	97	0	88	7
CFC-113	93	92	98	98	82	96	94

^a All values were read from the bar charts in the referenced report

^b 5:45:50 mixture of Butyl Cellosolve® (2-butoxyethanol or ethylene glycol monobutyl ether): isopropanol:water

^c 85:15 mixture of isopropanol: 2-butoxyethanol

^d 3M Product, C₆F₁₄

^e DuPont product, C₆F₁₂

* Presumably tricresylphosphate

** Although the report did not indicate it, one presumes that the weighing pans were weighed before they were contaminated.

produces similar results to CFC-113 when testing a limited number of real world samples." This is a fairly strong endorsement of the Butyl Cellosolve®/IPA mixture.

There are three factors that militate against the use of this material for NVR testing. First, the vapor pressure at room temperature is low, 0.6 Torr at 20°C.³¹ This means relatively long test times. The use of a mixture requires either developing a reliable vendor or vendors for the mixture, in the needed cleanliness, or for test laboratories to maintain inventories of two types of extremely pure solvents. Finally, and most significantly, Ross reported no TLV data. A vendor's MSDS reports TLV's of 25 ppm, with potential for skin adsorption (ACGIH value) and 50 ppm (OSHA value) for Butyl Cellosolve®.³¹

4.5 CFM Technologies Testing

Walker and Parker report the results of immersion cleaning tests to evaluate various solvents as alternatives to CFC's for cleaning.³² These tests used five model contaminants: lithium grease, rosin flux (MIL-F-14256), dioctyl phthalate, Desitin ointment, and cocoa butter.

Contaminants were coated onto watch glasses. The samples were immersed in the solvent at 50°C for 5 minutes. No agitation was applied. The extent of contaminant removal was evaluated gravimetrically. Table 9 presents the results of this work.

These results offer two points of interest to this work. First, the ethyl lactate solvent, which has received some publicity,³³ did not appear to perform too well. Second, a wide range of solvents appears to be successful at removing dioctyl phthalate. This supports our declining to use this commonly mentioned contaminant in our testing. (We preferred not to use this material on safety grounds. It is a suspected human carcinogen.)

Table 9. Immersion Test Results for 10 Solvents, Tested at 50°C

Solvent	Contaminant (% Remaining)				
	Lithium Grease	Desitin	Rosin	Diethyl Phthalate	Cocoa Butter
CFC-113	0.85	0.31	3.72	0.00	0.93
TCA	0.00	3.27	0.00	0.00	0.00
IPA	34.69	23.75	0.00	0.00	0.00
hexane	99.14	0.11	8.61	0.00	2.53
acetone	1.16	8.27	0.00	0.39	2.33
Ionox FC ^a	75.15	62.69	26.42	0.00	3.64
Purasolv EL ^b	61.96	83.61	36.39	36.97	0.00
Re-Entry KNI 200 ^c	4.44	0.00	0.00	0.00	0.00
Art-210 ^d	0.88	1.43	0.00	0.00	0.00
OS-10 ^e	4.44	0.49	99.91	0.00	1.05
Significant Difference ^f	15.48	16.03	8.54	23.71	13.74

^a described as "nonlinear alcohol"

^b ethyl lactate

^c terpene

^d terpene

^e volatile methyl silicone

^f the difference in % remaining required for two solvents to be statistically significantly different in cleaning ability

4.6 Aqueous NVR Determination

An aqueous nonvolatile residue removal and validation approach has attracted interest in the aerospace community.^{34,35,36} The aqueous NVR approach involves cleaning parts in distilled water using an ultrasonic bath, followed by measuring the total organic carbon (TOC) contained in the wash water. Using knowledge of the volume of wash water and area of the sample, combined with empirical calibration of the detector, allows one to compute the amount of residue cleaned from the sample.

The aqueous procedure is a promising substitute for CFC washing of robust hardware, particularly items intended for oxygen service. Indeed, NASA intends to alter cleaning specifications for some hardware to define an aqueous approach for cleaning and validation of some hardware.³⁶ However, the current aqueous procedure cannot replace the surface sampling wipe test. There are also substantial issues to address in considering the approach as a replacement for cleanroom NVR testing.

4.6.1 Surface Sampling

SD-TR-89-63 describes a test for determining the cleanliness of surfaces by solvent wiping and gravimetric analysis. This test is intended to be applicable to delicate spacecraft hardware. The aqueous approach described in reference 34 relies on putting the item to be tested in a heated, ultrasonically agitated bath. Alternatively, Allen et al. suggest,

For components too large to place in the ultrasonic bath, a hot water/steam impingement process will be evaluated...

Clearly, the aqueous process is not a suitable replacement for the SD-TR-89-63 wipe test for surface sampling of delicate hardware.

4.6.2 Clean Room Diagnosis

The aqueous NVR validation approach described in reference 34 may at some time be useful for clean room diagnosis, but will not be a "drop in" replacement for the method described in ASTM E 1235-88. The discussion presented below indicates some of the difficulties that would be involved.

The tests described in references 34 and 36 are performed at 52° and 70°C. ASTM E 1235-88 specifies that NVR samples should not be exposed to temperatures higher than 35° C. It is understandable that the authors would choose relatively high temperatures. The kinds of organic materials that they seek to clean from surfaces are not particularly soluble in water, and keeping the water warm will reduce the amount of dissolved CO₂. However, for clean room diagnosis, it needs to be demonstrated more clearly that the high temperature process does not result in the evaporative loss of some residue, leading to a false low test.

The detection approach used was to pyrolyze the water sample and detect the carbon dioxide. The amount of carbon dioxide produced is proportional to the amount of organic carbon in the NVR. However, as the authors point out, the proportionality constant varies with the stoichiometry of the residue mixture. Silicones, particularly potent NVR contaminants for bonding processes, have less carbon per unit weight than pure hydrocarbons. Therefore, for an unknown NVR composition, the relationship between NVR mass density and TOC will not be precise and may not be accurate.

One may certainly say that the same variability exists with a solvent rinse approach: various NVR materials will exhibit differing solubilities in the solvent. However, the absolute accuracy is not the only virtue of a replacement for the current NVR diagnosis. A replacement for ASTM E 1235-88 must also provide similar measurements of NVR for the same clean room conditions. Additional calibration of the TOC approach would be required to make that correlation.

Table 10 shows the cleanliness levels defined by MIL-STD-1246B.³⁷ USAF spacecraft typically require level A for spacecraft surfaces and for the Titan IV fairing. We are unfamiliar with any requirement more lenient than level F for flight hardware. ASTM E 1235-88 requires a blank (or intercept) NVR level of less than about 100 $\mu\text{g}/\text{ft}^2$. The required measurement precision is $\pm 10 \mu\text{g}$. The aqueous NVR determination results reported in reference 34 do not extend to the low NVR levels required. (See fig. 6 in reference 34.) The authors acknowledge that additional work will be required for the technique to be applied for these NVR levels.

ASTM E 1235-88 specifies that the NVR collected be retained for analysis, if needed. This is an important option. Analysis of the composition of the NVR, e.g., by infrared spectroscopy or GC/Mass Spectrometry, is often required either to ascertain the source of the contaminants (for remedial actions) or to evaluate the potential harmful effects of the contaminants. The extreme dilution of the NVR in water makes this kind of analysis difficult.

Table 10. Classification of Product Cleanliness Levels

Level	NVR Quantity (mg per sq. ft.)
A	LESS THAN 1.0
B	1.0 to 2.0
C	2.0 to 3.0
D	3.0 to 4.0
E	4.0 to 5.0
F	5.0 to 7.0
G	7.0 to 10.0

5.0 Laboratory Test Results

5.1 Solvent Availability

The first part of experimental testing was to ascertain the availability of solvents of suitable purity for NVR diagnosis. A review of organic chemical vendors revealed that ACS HPLC grade materials are available for both acetates (at < 3 ppm evaporation residue specification). The price for these solvents is approximately \$20 per liter.

Table 11 shows examples of laboratory tests, following the procedure in ASTM E 1235-88 used to evaluate the achieved cleanliness for some samples of the HPLC esters, compared to HPLC dichloromethane and "anhydrous" TCA.* Note that these data evaluate both the purity of the solvent and the "technique" of the experimenter.

Further review of the availability of solvents indicated a vendor of high purity chemicals that provides ethyl acetate in several grades that meet the general requirement of these tests of evaporation residue of ~1 ppm. While this report does endorse a particular vendor for future government procurements, we do indicate that Baxter B&J brand ethyl acetate has been found suitable for this testing. Appendix 2 presents Baxter B&J and Aldrich Chemical Co. solvent specifications from their product literature.

Table 11. Solvent NVR Tests, 60 ml Samples, As-Received Solvents

Solvent	Test 1				Test 2			
	Residue (g)	ppm	Mean	Std. Dev.	Residue (g)	ppm	Mean	Std. Dev.
dichloromethane	0.00007	0.9	0.9	0.1	0.00013	1.6	2.0	0.31
	0.00008	1.0			0.00019	2.4		
	0.00006	0.8			0.00016	2.0		
ethyl acetate	0.00026	4.8	4.0	0.68	0.00003	0.6	0.6	0.00
	0.00017	3.1			0.00003	0.6		
	0.00022	4.1			0.00003	0.6		
methyl acetate	0.00002	0.4	1.6	1.2	0.00008	1.4	0.7	0.58
	0.00007	1.3			0.00000	0.0		
	0.00018	3.2			0.00004	0.7		
trichloroethane	0.00034	4.2	3.5	0.56	0.00033	4.1	4.4	0.99
	0.00028	3.5			0.00046	5.7		
	0.00023	2.9			0.00027	3.4		

* Solvents used in these tests were obtained from Aldrich Chemical Co.

5.2 Intentional Contamination: NVR Wipe Test

Initially, testing was undertaken to evaluate candidate solvents in the wipe test, as well as the ASTM witness plate test.

Sample plates were prepared that could be precontaminated with chosen materials to test the effectiveness of candidate replacement solvents. The plates were fabricated from aluminum, with 1 ft² recesses into which contaminant solutions were poured. The plates were leveled with micrometer screws so that as the contaminant solution dried, a nearly uniform film of contaminant residue was left. Figure 8 shows a drawing of the sample plates fabricated for this work.

Tests were run using cotton wipers from Thermo Analytical Laboratory. In performing these tests, it was observed that the methyl acetate evaporated very rapidly, while the wipe was being performed. This observation, and the fact that methyl acetate is somewhat more toxic than the other solvents, militate against its use for the wipe test.

Table 12 shows the results of one test in which the wipe witness plates were contaminated with the hydrocarbon squalane. It is immediately obvious that the background levels (NVR from the wiper) are unacceptably high from the two acetate solvents.

Table 12. Test Results for NVR Wipe of Test Samples Precontaminated with Squalane

Solvent	Applied NVR (g)	Sample NVR (g)	Blank NVR (g)	Test NVR (g)
methyl acetate	0.00364	0.00265	0.00110	0.00155
ethyl acetate	0.00362	0.00306	0.00218	0.00088
"NVR" solvent	0.00369	0.00514	0.00209	0.00305

Similar difficulties were observed in other of our tests. The problem of NVR from wipers is well recognized as a source or error in this sort of testing. Parks reported the same concern in his solvent replacement testing.³⁸ This problem can be remedied by proper pre-test extraction of the wipers with the solvent to be used during testing.³⁹

This subject is currently being addressed in a series of "round robin" tests guided by ASTM Committee E-21 in an attempt to revise standard E1560-93 entitled "Standard Test Method for Gravimetric Determination of Nonvolatile Residue from Cleanroom Wipers."⁴⁰ We have received a set of the wipers from this "round robin."

Since the purpose of the current effort was to identify solvents, rather than appropriate wipers, we decided to discontinue wipe testing as a means of intercomparison of solvents.

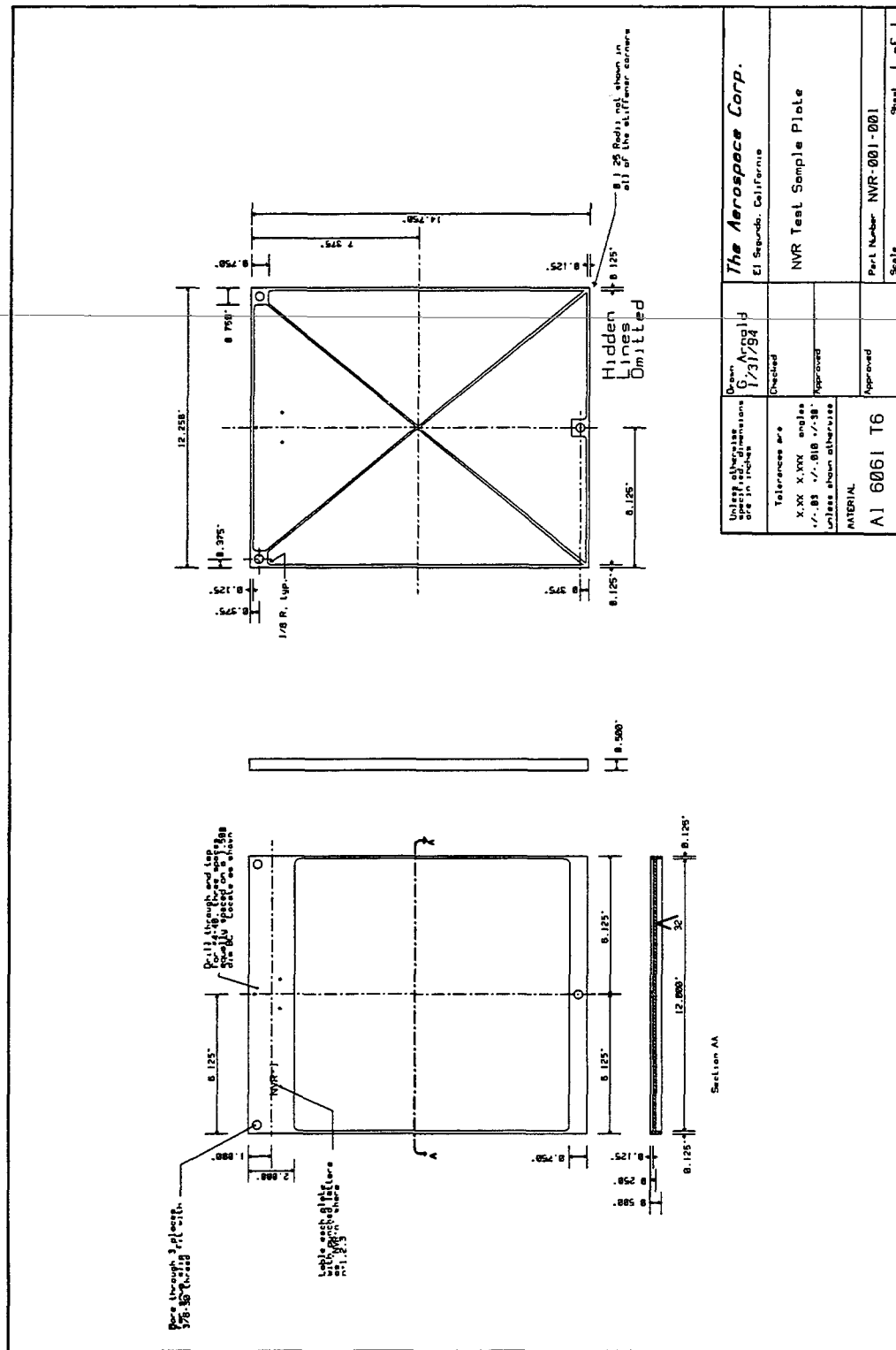


Figure 8. Wipe test witness plate. Not shown to scale.

5.3 Contamination Test (ASTM E 1235)

5.3.1 Adventitious Contamination

The suitability of the candidate replacement solvents was initially evaluated using adventitious contaminants obtained by exposing witness samples to an uncontrolled environment.

Table 13 presents results of a single ASTM E 1235-88 stainless steel witness plates test for samples that were exposed in The Aerospace Corp. machine shop for about 1 month, then bagged together for ~3 months. The agreement between the standard solvent and ethyl acetate results is strikingly good.

This kind of testing requires long exposure of sample plates without always producing a reliable degree of contamination. (Witness the low NVR found in a machine shop!) Therefore, the remainder of our testing was done with intentionally contaminated ASTM E 1235 witness plates.

Table 13. ASTM E 1235 Test Comparison Between Dichloromethane and Ethyl Acetate

Measured Mass (g)	Solvent	
	Dichloromethane	Ethyl Acetate
Sample	0.00093	0.00147
Blank	0.00029	0.00072
NVR	0.00064	0.00075

5.3.2 Precontaminated Stainless Steel Witness Plates

ASTM E 1235-88 witness plates were contaminated with various materials likely to be of concern, particularly in Titan IV processing environments. Materials were weighed in pyrex beakers and diluted in a volatile solvent. The solutions were allowed to evaporate on previously cleaned witness plates. Then the procedures called out in ASTM E 1235-88 were followed to evaluate the effectiveness of the solvent, with two exceptions.

First, the solvent evaporation technique used was method A as described in SD-TR-89-63, vacuum furnace evaporation. Several tests using the free ambient evaporation described in ASTM E 1235 resulted in substantial water condensation into the sample, even in a controlled, clean room environment. Second, a vacuum desiccator was not used to store the samples before weighing.

Table 14 shows the contaminants evaluated. Note that the hydrocarbon squalane was used because Barrows identified it as a significant component in lubricants used in Titan IV fairing processing. The BOE Lube material was also supplied by Martin CCAS personnel to assist in this testing.²³

Table 14. Materials Used in ASTM E 1235-88 Tests

Contaminant	Titan IV Material
hexadecanol (cetyl alcohol)	✓
squalane	✓
BOE Lube	✓
tetraphenyl dimethyl disiloxane	

The results of these tests are shown in Figure 9 through Figure 12. These figures plot the contaminant recovery from each set of tests, which is defined as

$$R(\%) = \frac{m_r - m_b}{m_c} \times 100 \quad (6)$$

where m_r is the mass of residue detected, m_b is the mass of the solvent blank, and m_c is the mass of the preweighed contaminant. The figures reveal that the combined scatter in these measurements is around $\pm 10\%$. The primary sources of error are the multiple transfers of residue required to perform these tests and scatter in the solvent blank correction. In most cases, the agreement among ethyl acetate, methyl acetate, and dichloromethane was quite good, indeed. One of the methyl acetate measurements with squalane is out of family. Those were among the first tests, when experimental technique was still developing.

Ethyl acetate and methyl acetate appear to perform equally well. It was observed in various of the tests that the high free evaporation rate of methyl acetate can potentially cause problems in performing the tests. This characteristic, coupled with the greater toxicity of methyl acetate, indicate that ethyl acetate is a better choice for an NVR test solvent.

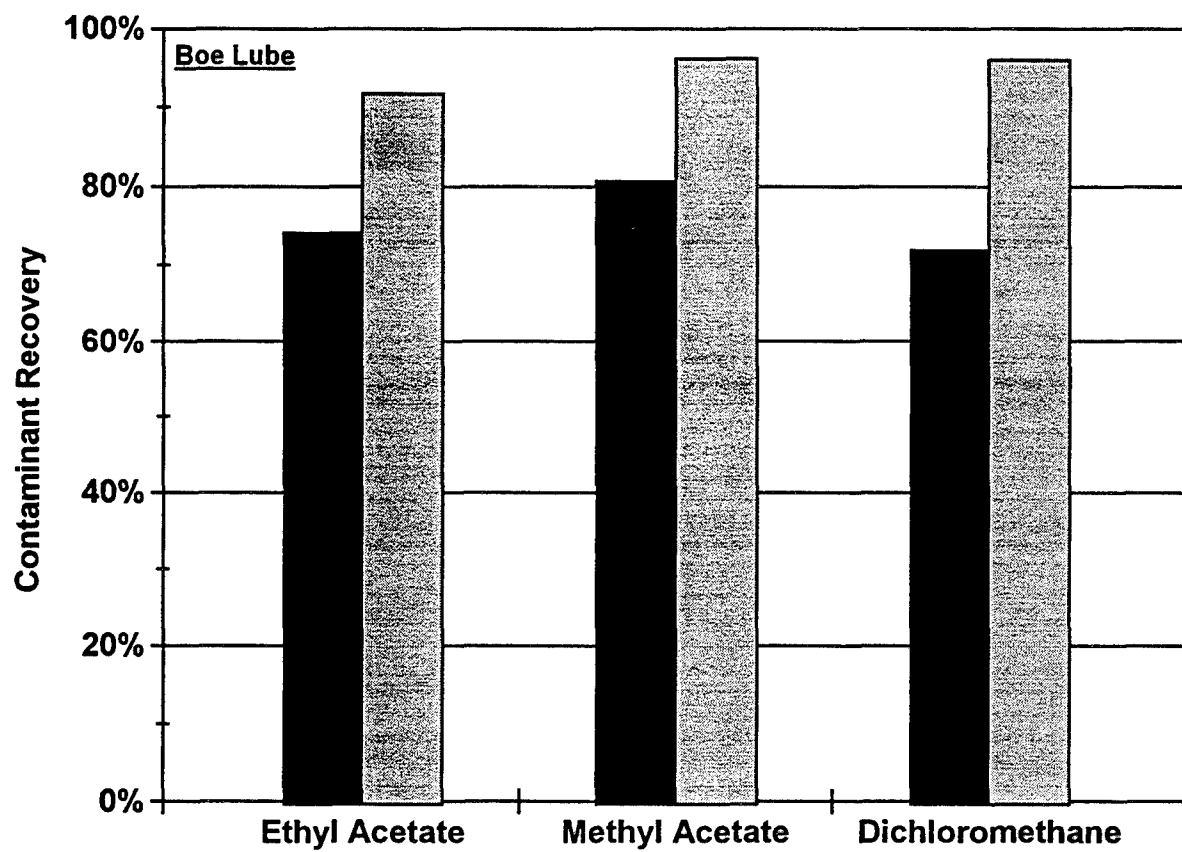


Figure 9. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with BOE Lube.

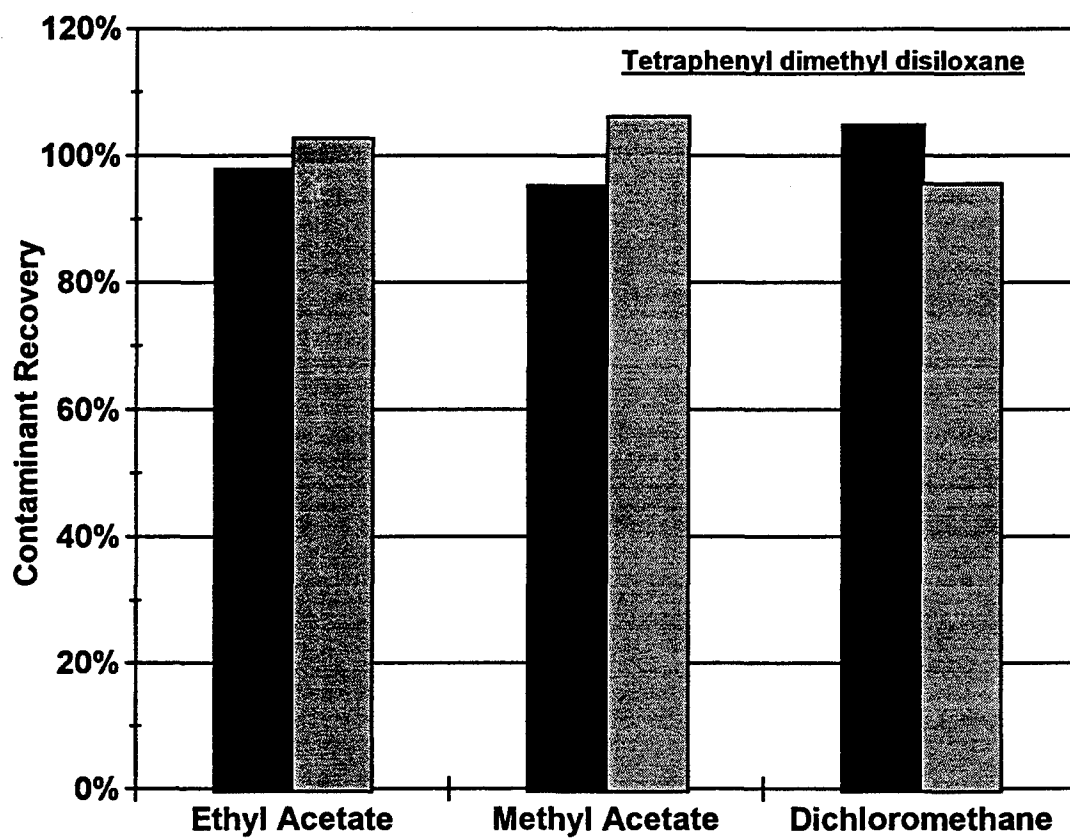


Figure 10. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with tetraphenyl dimethyl disiloxane.

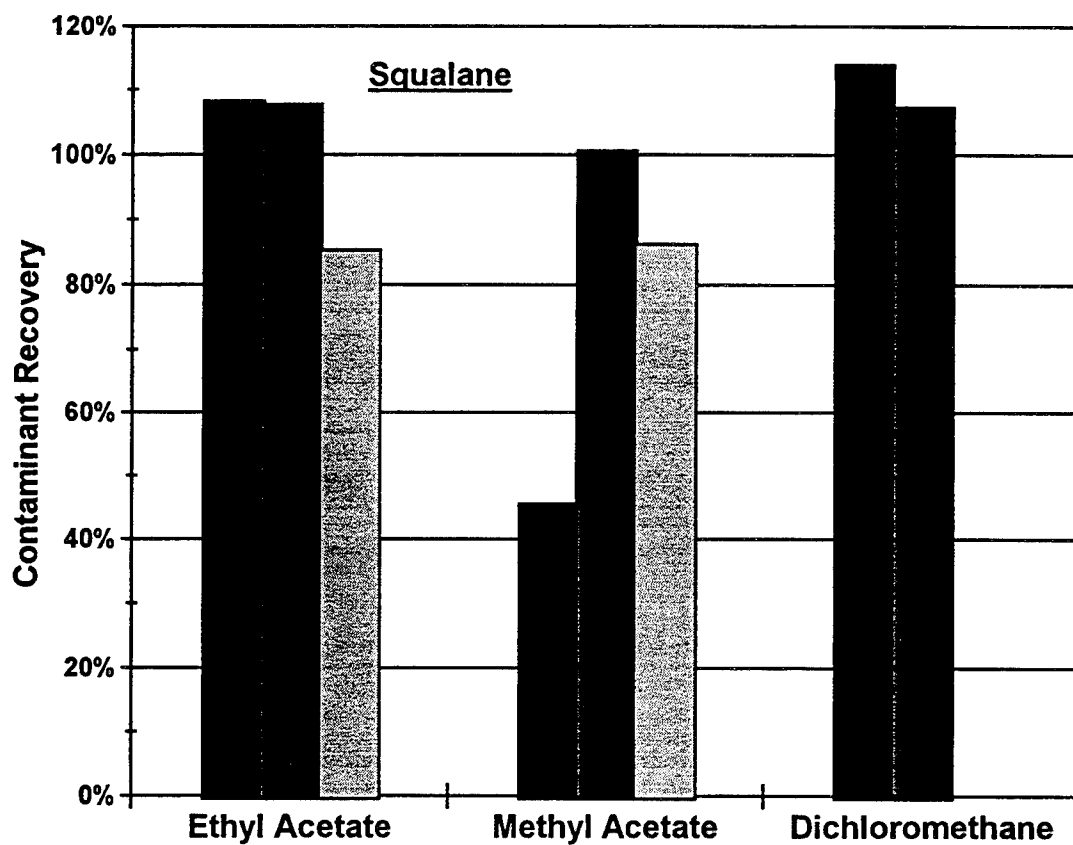


Figure 11. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with squalane.

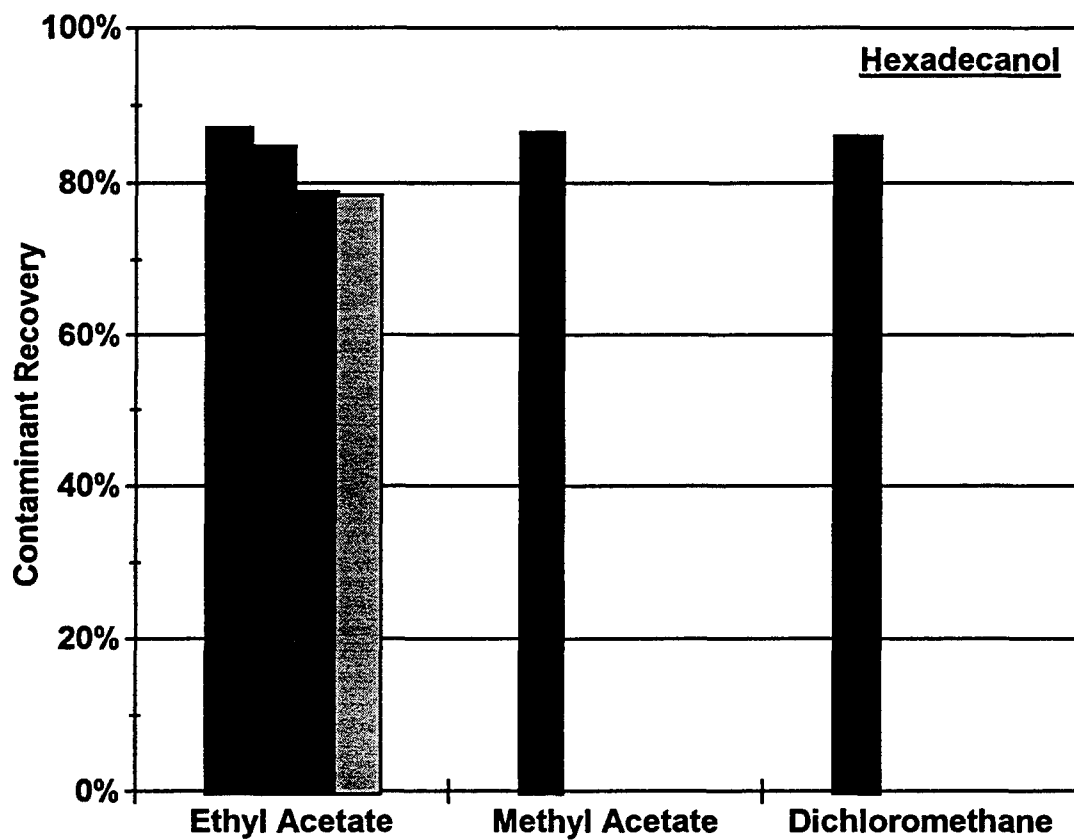


Figure 12. Percent contaminant recovery for ASTM E 1235-88 stainless steel witness plates precontaminated with hexadecanol.

6.0 Summary

The standard tests for determining nonvolatile residue accretion on spacecraft surfaces and in clean processing facilities rely on the use of halogenated solvents that are targeted for elimination because of their toxic or ozone-depleting natures. A literature-based screening survey for candidate replacement solvents and laboratory test data using both model and adventitious contaminants, from The Aerospace Corporation, and elsewhere, have been described.

6.1 NVR Solvent Replacement Recommendations

Two clear candidates for a replacement NVR solvent emerge from the testing reviewed and reported here: ethyl acetate and ethyl acetate/cyclohexane azeotrope. For laboratory operations that must rely on procuring high purity solvents, pure ethyl acetate is recommended. For large laboratories that are equipped to purify their own solvents, the mixture is a good option. These solvents are recommended for general NVR evaluation. They are not expected to be suitable for NVR evaluation or cleaning when it is known that perfluorinated greases and oils are major contaminants, but it should be noted that neither are the TCA/EtOH or methylene chloride solvents.

A concern over release of volatile organic compounds, particularly at the WR, may require that the substitute solvents be contained. Testing done in this laboratory used "Method A" from the wipe test procedure for evaporation of the solvent. This method uses a vacuum furnace to facilitate evaporation and cold traps to collect the solvent. Method B, free evaporation in an exhausted fume hood, is currently permitted under the Titan IV contamination control plans.^{3,4} It may be desirable to delete option B from the Titan IV procedures.

6.2 Technology Insertion

Changing the Titan IV and Atlas contamination control plans to allow new solvents in place of the NVR solvent blend for the wipe test requires negotiations between the USAF and the appropriate contractors. To effect a change in solvent utilization will require agreements with the ER and WR Air Force laboratories where the analyses are performed. To facilitate these discussions, we will transmit this report (upon its clearance by SMC) to the ER and WR site contractors, Air Force analytical laboratories, and to Martin Marietta Denver contamination control specialists.

The ASTM E 1235-88 test standard can officially be altered only by the ASTM. The committee responsible for this standard is E-21 on Space Simulation. Upon clearance of this report by SMC, it will be communicated to Mr. Robert G. Moss of Space Systems/Loral, the ASTM committee member who has primary responsibility for updates of the relevant standards. Internal communication of this memorandum to Mr. E.N. Borson, a member of the E21 committee will start that process. Likewise, the results of Martin Marietta and Lockheed tests described above should be communicated to the ASTM as soon as possible.

6.3 Further Test Needs

6.3.1 Wipers

It is well known that the inherent contamination from wipers used for NVR diagnosis can interfere with accurate testing. Changing solvents in the NVR test procedure means that previously acceptable wiper materials may no longer be appropriate. It is incumbent on each laboratory that undertakes NVR wipe analysis to validate that the wipers used have acceptable levels and variability of inherent NVR and to preclean the wipers, if necessary.

The current round-robin in support of modification of ASTM E1560 should provide valuable information on this subject. Aerospace results from this testing will be reported in the future.

6.3.2 Evaporation Techniques

The solvents recommended for NVR analysis are not ODC's, but they are volatile hydrocarbons. ASTM Committee E21 is currently evaluating alternative means for atmospheric pressure evaporation of the solvent, that permit solvent capture.⁴⁰ Barrows has reported testing of a computer controlled vacuum rotary evaporator for accelerated solvent reduction.³⁹ These efforts should lead to further improvements in accuracy and decreased environmental concern for these NVR tests.

6.3.3 Materials Compatibility

Before ethyl acetate is used in the NVR wipe test, its compatibility with the surface in question needs to be verified by the organizations performing the tests. King and Giordano have reported some compatibility testing. (See above.) To supplement our existing library resources, information on additional data bases on solvent substitution and materials compatibility have been requested from the National Center for Manufacturing Science⁴¹ and the Idaho National Energy Laboratories.⁴²

32. A.E. Walker and J.W. Parker, "Selecting and Handling CFC-Alternative Critical Cleaning Solvents," *Microcontamination*, Vol. 12, no. 4, pp 27-33, April 1994.
33. E.A. Hill and K.D. Carter, "Using Ethyl Lactate for Precision Cleaning of Metal Surfaces," *Microcontamination*, November 1993, p. 27.
34. G.J. Allen, C.W. Hoppesch, R.S. Johnson, and M.D. Buckley, "Aqueous Nonvolatile Residue Validation of Precision Cleaned Hardware," *Alternatives to Chlorofluorocarbon Fluids in the Cleaning of Oxygen and Aerospace Systems and Components*, ASTM STP 1181, Coleman J. Bryan and Karen Gebert Thompson, ed., American Society for Testing and Materials, Philadelphia, 1993. (PREPRINT supplied by N. Keegan, The Aerospace Corporation.)
35. G.J. Allen, et al., *Methods for Using Water in Lieu of Chlorofluorocarbon 113 for Determining the Non-Volatile Residue Level on Precision Cleaned Hardware: Phase 1- Feasibility Testing*, Chlorofluorocarbon Replacement Chemical Working Group, Materials Science Laboratory, NASA Kennedy Space Center, FL, 7 January 1992.
36. G. Allen, *Aqueous Cleaning and Verification Processes for Precision Cleaning of Small Components*, Aerospace Environmental Technology Conference, Huntsville, AL, 10-11 August 1994.
37. *Military Standard Product Cleanliness Levels and Contamination Control Plan*, MIL-STD-1246B, Department of Defense, Washington, DC, 4 September 1987.
38. A. Parks, Lockheed Missiles and Space Co., private communication.
39. R. Barrows, "NVR Measurement Technique," Preliminary, Martin Marietta Corp., 14 September 1993.
40. E.N. Borson, The Aerospace Corporation, private communication.
41. M. Wixom, National Center for Manufacturing Science, private communication.
42. K. Twitchell, Idaho National Energy Laboratories, private communication.

Appendix A: Hansen Parameters for Various Solvents

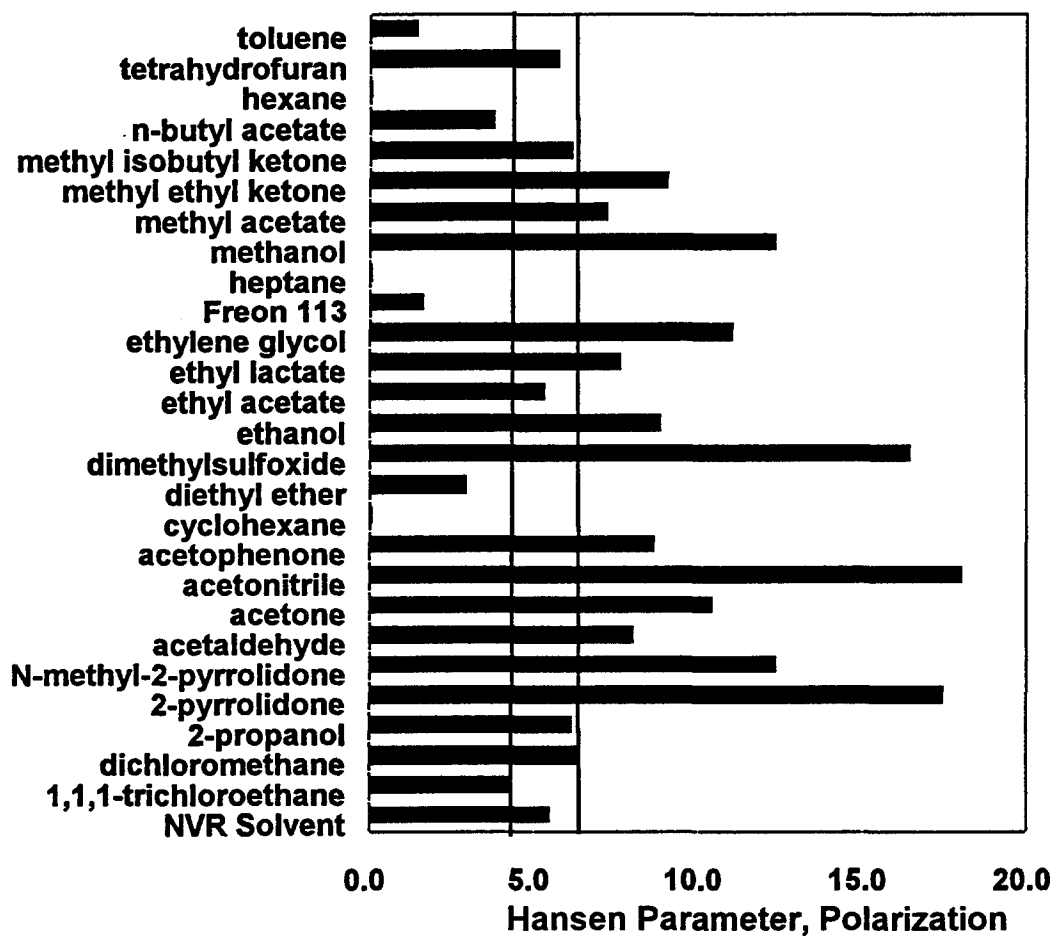


Figure A1. Hansen polarization force parameter (MPa)^{1/2} for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.

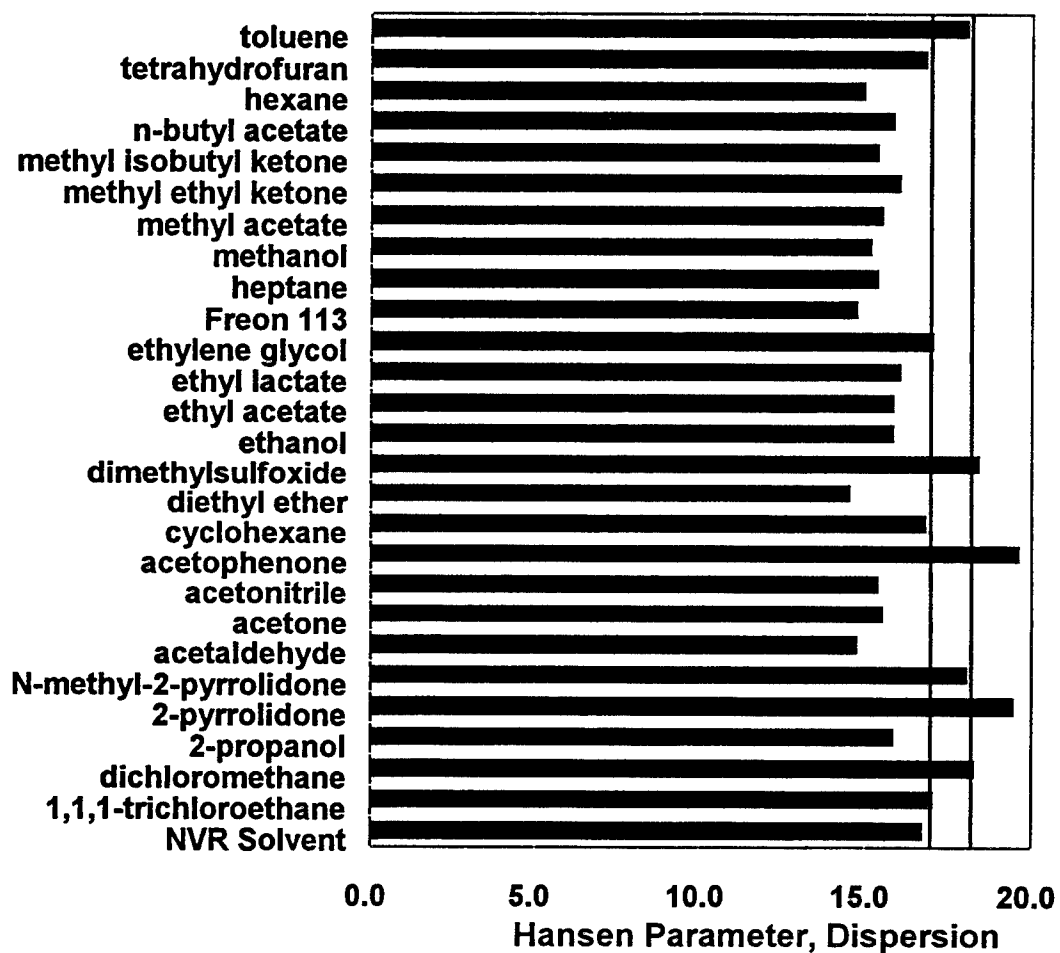


Figure A2. Hansen parameter for dispersion (MPa)^{1/2} for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.

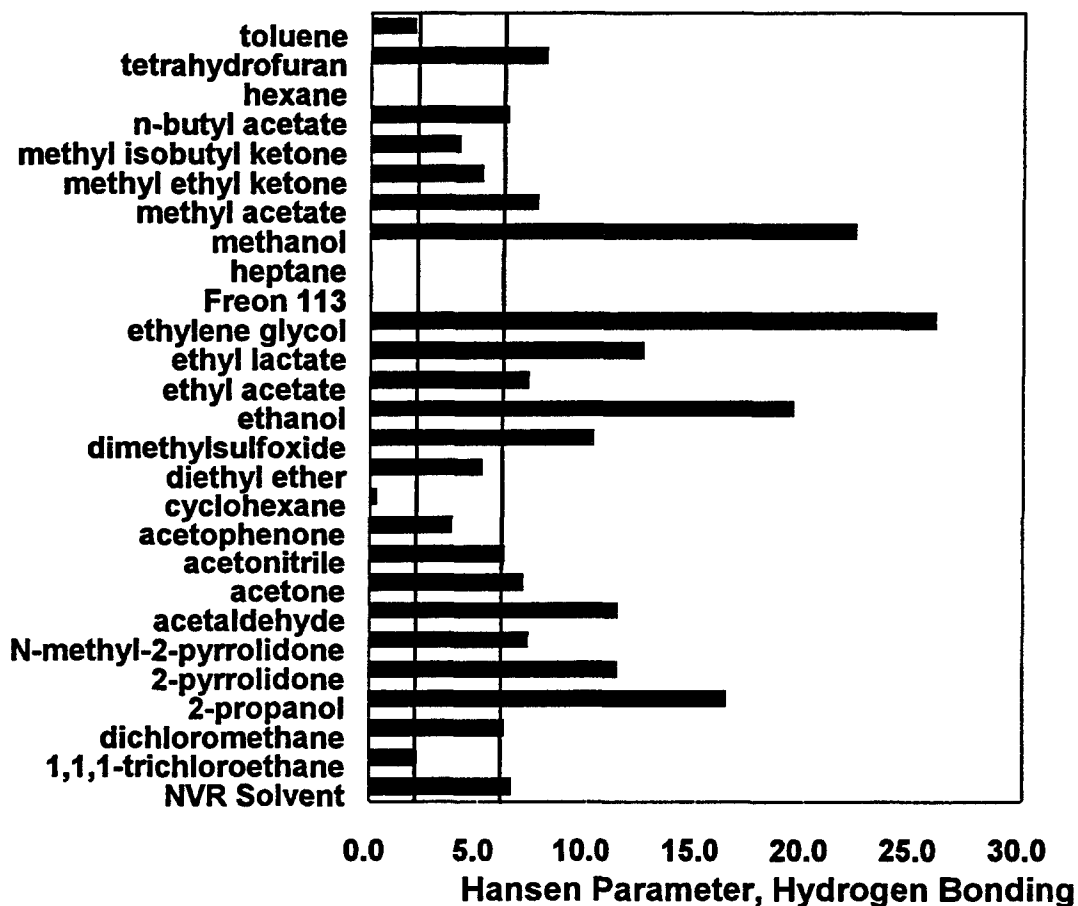


Figure A3. Hansen parameter for hydrogen bonding (MPa)^{1/2} for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.

Appendix B: Specifications of Commercial Ethyl Acetate

B.1 Baxter (Burdick and Jackson)

Manufactured by:

Baxter Diagnostics, Inc
Burdick and Jackson
1953 South Harvey St.
Muskegon, MI 49442

Distributed by:

Baxter Diagnostics, Inc.
Scientific Products
1430 Waukegan Rd
McGraw Park, IL 60085-6787
(708) 689-8410

Specifications, from Burdick and Jackson product information entitled High Purity Solvents and Products for Chromatography.

ETHYL ACETATE (CARBONYL-FREE)

B&J BRAND

For HPLC, GC, Spectrophotometry

UV Absorbance

Wavelength (nm)	Maximum Absorbance
256	1.000
275	0.005
300	0.005

Water (Max) 0.05 %
Refractive index at 20°C 1.3721 ± 0.0003
Residue (Max) 1 mg/liter [equivalent to 1.11 ppm]
GC Purity (Min) 99.9 %
Color with sulfuric acid Passes Test
Substances reducing permanganate Passes Test

B.2 Aldrich Chemical Company

Aldrich Chemical Company, Inc.
1001 West Saint Paul Avenue
Milwaukee, WI 53233
(800)-558-9160

Specifications from Aldrich Catalog Handbook of Fine Chemicals, 1992-1993.

ETHYL ACETATE (HPLC Grade)
Aldrich

UV Absorbance

Wavelength (nm)	Maximum Absorbance
254	1.0
263	0.05
400-275	0.01

Water (Max) 0.05%
Refractive index at 20°C 1.3720
Residue (Max) 0.0003% [3 ppm]
Purity 99.8%

Appendix C: Materials Safety Data Sheet for Ethyl Acetate



chemists helping chemists in research & industry

aldrich chemical co., inc.

P.O. Box 355, Milwaukee, Wisconsin 53201 USA

Telephone: (414) 273-3850
TWX: (910) 262-3052 Aldrichem
Telex: 26 843 Aldrich MI
FAX: (414) 273-4979

ATTN: SAFETY DIRECTOR
THE AEROSPACE CORPORATION

ATTN L U TOLENTINO/H2/359
ENVIRONMENTAL SAFETY REP
P O BOX 92957
LOS ANGELES CA 90009-2957

DATE: 11/03/93
CUST#: 100536
PC#: 58331-H

M A T E R I A L S A F E T Y D A T A S H E E T PAGE 1

SECTION 1. - - - - - CHEMICAL IDENTIFICATION- - - - -

PRODUCT #: 270520 NAME: ETHYL ACETATE, 99.8%, HPLC GRADE

SECTION 2. - - - - - COMPOSITION/INFORMATION ON INGREDIENTS - - - - -

CAS #:141-79-6
MF: C4H8O2

SYNONYMS

ACETIC ETHER * ACETIDIN * ACETOXYETHANE * AETHYLACETAT (GERMAN) *
ESSIGESTER (GERMAN) * ETHYLACETAAT (DUTCH) * ETHYL ACETATE * ETHYL
ACETATE (ACGIH, DOT, OSHA) * ETHYL ACETIC ESTER * ETHYLE (ACETATE D*)
(FRENCH) * ETHYLESTER KYSELINY OCTOVE (CZECH) * ETHYL ETHANOATE *
ETILE (ACETATO DI) (ITALIAN) * OCTAN ETYLU (POLISH) * RCRA WASTE
NUMBER U112 * U1173 (DOT) * VINEGAR NAPHTHA *

SECTION 3. - - - - - HAZARDS IDENTIFICATION - - - - -

LABEL PRECAUTIONARY STATEMENTS

FLAMMABLE (USA DEFINITION)

HIGHLY FLAMMABLE (EUROPEAN DEFINITION)

IRRITANT

IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.

TARGET ORGAN(S):

LIVER

KIDNEYS

KEEP AWAY FROM SOURCES OF IGNITION. NO SMOKING.

IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF

WATER AND SEEK MEDICAL ADVICE.

WEAR SUITABLE PROTECTIVE CLOTHING.

PROTECT FROM MOISTURE.

SECTION 4. - - - - - FIRST-AID MEASURES- - - - -

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF
WATER FOR AT LEAST 15 MINUTES.

IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS
AMOUNTS OF WATER.

IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.

CONTINUED ON NEXT PAGE

Belgium
Aldrich Chemie
K. Cardonck, 8
B-2880 Bornem
Telephone: 038991301
FAX: 038991311

France
Aldrich-Chemie S.A.R.L.
B.P. 701
38297 Saint Quentin Fallavier
Cedex
Telephone: 74822800
Telex: 308215 Aldrich F
FAX: 74956808

Italy
Aldrich Chimica
Via Galvani, 154
20151 Milano
Telephone: 0233417370
FAX: 0238010737

Japan
Aldrich Japan
Kyoto Bldg. Shinjuku
10 Kamada-Makurashi
Chiyoda-Ku, Tokyo
Telephone: 0332580155
FAX: 0332580157

Spain
Aldrich Quimica
Apt de Correos 161
28100 Alcobendas (Madrid)
Telephone: 3416619977
Telex: 27189 SACS-E
FAX: 3416618084

United Kingdom
Aldrich Chemical Co., Ltd
The Old Brickyard, New Road
Gillingham, Dorset SP8 4R
Telephone: 0747822211
Telex: 417238 Aldrich G
FAX: 0747823779

Germany
Aldrich-Chemie GmbH & Co. KG
W-7924 Steinheim
Telephone: 07329870
Telex: 714838 Aldin D
FAX: 0732987139/239

Switzerland
Aldrich Chemie
Industrieweg 25
P.O. Box 260
CH-9470 Buchs
Telephone: 08569723
FAX: 08567420

Australia
Aldrich Chemical
Unit 2
10 Ansett Ave.
Castle Hill NSW 2154
Telephone: 028999977
FAX: 028999742



chemists helping chemists in research & industry

aldrich chemical co., inc.

P.O. Box 355, Milwaukee, Wisconsin 53201 USA

Telephone: (414) 273-3850
TWX: (910) 262-3052 Aldrichem
Telex: 26 843 Aldrich MI
FAX: (414) 273-4979

M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 2

PRODUCT #: 270520
MF: C4H8O2

NAME: ETHYL ACETATE, 99.8%, HPLC GRADE

CUST#: 100536
PO#: 58331-H

IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.
WASH CONTAMINATED CLOTHING BEFORE REUSE.

SECTION 5. - - - - - FIRE FIGHTING MEASURES - - - - -

EXTINGUISHING MEDIA

CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.

WATER MAY BE EFFECTIVE FOR COOLING, BUT MAY NOT EFFECT EXTINGUISHMENT.

SPECIAL FIREFIGHTING PROCEDURES

FLAMMABLE LIQUID.

WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO

PREVENT CONTACT WITH SKIN AND EYES.

USE WATER SPRAY TO COOL FIRE-EXPOSED CONTAINERS.

UNUSUAL FIRE AND EXPLOSIONS HAZARDS

VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND

FLASH BACK.

CONTAINER EXPLOSION MAY OCCUR UNDER FIRE CONDITIONS.

FORMS EXPLOSIVE MIXTURES IN AIR.

SECTION 6. - - - - - ACCIDENTAL RELEASE MEASURES - - - - -

EVACUATE AREA.

SHUT OFF ALL SOURCES OF IGNITION.

WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY

RUBBER GLOVES.

COVER WITH AN ACTIVATED CARBON ADSORBENT, TAKE UP AND PLACE IN CLOSED

CONTAINERS. TRANSPORT OUTDOORS.

VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

SECTION 7. - - - - - HANDLING AND STORAGE - - - - -
REFER TO SECTION 8.

ADDITIONAL INFORMATION

ETHYL ACETATE IS SLOWLY DECOMPOSED BY MOISTURE. IT REACTS EXPLOSIVELY
WITH LITHIUM ALUMINUM HYDRIDE.

CONTINUED ON NEXT PAGE

Belgium
Aldrich Chemie
4, Clorenpoort, 8
B-2880 Borrem
Telephone: 038991301
FAX: 038991311

France
Aldrich-Chemie S.A.S.
B.P. 701
38297 Saint Quentin Fallavier
Cedex
Telephone: 74822800
Telex: 308215 Aldrich F
FAX: 74956808

Italy
Aldrich Chimica
Via Galarate, 154
20151 Milano
Telephone: 0233417370
FAX: 0238010737

Japan
Aldrich Japan
Kyodo Bldg. Shinkansai
10 Kanda-Misakicho
Chiyoda-Ku, Tokyo
Telephone: 0332580155
FAX: 0332580157

Spain
Aldrich Quimica
Apt. de Correos 161
28100 Alcobendas (Madrid)
Telephone: 3416619977
Telex: 22189 SAQ/54
FAX: 3416618084

United Kingdom
Aldrich Chemical Co., Ltd.
The Old Brickyard, New Road
Gillingham, Dorset SP8 4JK
Telephone: 0747822211
Telex: 417738 Aldrich G
FAX: 0747823779

Germany
Aldrich-Chemie GmbH & Co. KG
W-7924 Steinheim
Telephone: 07329870
Telex: 714838 Aldin D
FAX: 0732987139/239

Switzerland
Aldrich Chemie
Industriemstrasse 25
P.O. Box 260
CH-9470 Buchs
Telephone: 08569723
FAX: 08567420

Australia
Aldrich Chemical
Unit 2
10 Anella Ave.
Castle Hill NSW 2154
Telephone: 028999977
FAX: 028999742



chemists helping chemists in research & industry

aldrich chemical co., inc.

P.O. Box 355, Milwaukee, Wisconsin 53201 USA

Telephone: (414) 273-3850
TWX: (910) 262-3052 Aldrichem
Telex: 25 843 Aldrich MI
FAX: (414) 273-4979

M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 3

PRODUCT #: 270520
MF: C4H8O2

NAME: ETHYL ACETATE, 99.8%, HPLC GRADE

CUST#: 100536
PO#: 58331-H

SECTION 8. - - - - - EXPOSURE CONTROLS/PERSONAL PROTECTION- - - - -

CHEMICAL SAFETY GOGGLES.
RUBBER GLOVES.
SAFETY SHOWER AND EYE BATH.
USE ONLY IN A CHEMICAL FUME HOOD.
NIOSH/MSHA-APPROVED RESPIRATOR IN NONVENTILATED AREAS AND/OR FOR
EXPOSURE ABOVE THE ACGIH TLV.
DO NOT BREATHE VAPOR.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
IRRITANT.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
STORE IN A COOL DRY PLACE.

SECTION 9. - - - - - PHYSICAL AND CHEMICAL PROPERTIES - - - - -

APPEARANCE AND ODOR
COLORLESS LIQUID
BOILING POINT: 76.5 C TO 77.5 C
MELTING POINT: -84 C
FLASHPOINT 26 F BY:
AUTOIGNITION TEMPERATURE: 905 F
UPPER EXPLOSION LEVEL: 11.5% 38 C
LOWER EXPLOSION LEVEL: 2.2% 38 C
VAPOR PRESSURE: 73MM 20 C
VAPOR DENSITY: 3
SPECIFIC GRAVITY: 0.902

SECTION 10. - - - - - STABILITY AND REACTIVITY- - - - -

STABILITY
STABLE.
INCOMPATIBILITIES
OXIDIZING AGENTS

CONTINUED ON NEXT PAGE

France
Aldrich-Chemie S.A.S.
B.P. 701
38297 Saint Quentin Fallavier
Cedex
Telephone: 74822800
Telex: 308215 Aldrich F
FAX: 74956808

Belgium
Aldrich-Chemie
K. Cardoenstr. 8
B-2880 Bornem
Telephone: 038991301
FAX: 038991311

Italy
Aldrich-Chemie
Via Galvani, 154
20151 Milano
Telephone: 0233417370
FAX: 0238010737

Japan
Aldrich Japan
Kyodo Bldg. Shinkawa
10 Kanda-Mitsuchino
Chiyoda-Ku, Tokyo
Telephone: 0332580155
FAX: 0332580157

Spain
Aldrich-Chemie
Apt. de Correos 161
28100 Alcobendas (Madrid)
Telephone: 3416619977
Telex: 23189 SAQS-E
FAX: 3416618084

United Kingdom
Aldrich Chemical Co., Ltd.
The Old Brickyard, New Road
Gillingham, Dorset SP9 4JA
Telephone: 0747822211
Telex: 417238 Aldrich G
FAX: 0747823779

Germany
Aldrich-Chemie GmbH & Co. KG
W-7924 Steinheim
Telephone: 07329870
Telex: 714838 Aldrich D
FAX: 0732987139/239

Switzerland
Aldrich-Chemie
Industriestrasse 25
P.O. Box 260
CH-9470 Buchs
Telephone: 08569723
FAX: 08567420

Australia
Aldrich Chemical
Unit 2
10 Ananda Ave.
Castle Hill NSW 2154
Telephone: 0289999977
FAX: 0289999742



chemists helping chemists in research & industry

aldrich chemical co., inc.

P.O. Box 355, Milwaukee, Wisconsin 53201 USA

Telephone: (414) 273-3850
TWX: (910) 262-3052 Aldrichem
Telex: 26 843 Aldrich MI
FAX: (414) 273-4979

M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 4

PRODUCT #: 270520
MF: C4H8O2

NAME: ETHYL ACETATE, 99.8%, HPLC GRADE

CUST#: 100536
PO#: 58331-H

BASES
ACIDS
MOISTURE
HEAT
SENSITIVE TO MOISTURE
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
TOXIC FUMES CF:
CARBON MONOXIDE, CARBON DIOXIDE
HAZARDOUS POLYMERIZATION
WILL NOT OCCUR.

SECTION 11. - - - - - TOXICOLOGICAL INFORMATION - - - - -

ACUTE EFFECTS

MAY BE HARMFUL BY INHALATION, INGESTION, OR SKIN ABSORPTION.
CAUSES SKIN IRRITATION.
VAPOR OR MIST IS IRRITATING TO THE EYES, MUCOUS MEMBRANES AND UPPER
RESPIRATORY TRACT.
CAN CAUSE CNS DEPRESSION.
PROLONGED EXPOSURE CAN CAUSE:
NAUSEA, HEADACHE AND VOMITING
NARCOTIC EFFECT
ANEMIA
TARGET ORGAN(S):
LIVER, KIDNEYS
CENTRAL NERVOUS SYSTEM
BLOOD

RTECS NO: AH5425000
ACETIC ACID, ETHYL ESTER

IRRITATION DATA
EYE-HMN 400 PPM

TOXICITY DATA
ORL-RAT LD50: 5620 MG/KG
ORL-MUS LD50: 4100 MG/KG
IHL-MUS LC50: 45 GM/M3/2H
IPR-MUS LD50: 709 MG/KG
SCU-CAT LD50: 3 GM/KG
ORL-RBT LD50: 4935 MG/KG
SKN-RBT LD50: >20 GM/KG
ORL-GPG LD50: 5500 MG/KG

JIHTAB 25,282,43

YKYUA6 32,1241,81
GISAAA 48(4),66,83
85GMAT -,65,82
SCCUR* -,5,61
AGGHAR 5,1,33
IMSUA1 41,31,72
UCDS** 10,4,68
GISAAA 48(4),66,83

CONTINUED ON NEXT PAGE

Belgium
Aldrich Chemie
E. Cardonpoen, 8
B-2880 Bornem
Telephone: 038991301
FAX: 038991311

France
AldrichChime S a r l
8 P. 701
38297 Saint Quentin Fallavier
Cedex
Telephone: 74822800
Telex: 308215 Aldrich F
FAX: 74956828

Italy
Aldrich Chimica
Via Gallarate, 154
20151 Milano
Telephone: 0233417370
FAX: 0238010737

Japan
Aldrich Japan
Kyosai Bldg. Shinkansai
10 Kanda-Mitsukicho
Chiyoda-Ku, Tokyo
Telephone: 0332580155
FAX: 0332580157

Spain
Aldrich Quimica
Apt. de Correos 161
28100 Alcobendas (Madrid)
Telephone: 3416619977
Telex: 27189 SAOS-E
FAX: 3416618084

United Kingdom
Aldrich Chemical Co., Ltd.
The Old Brickyard, New Road
Gillingham, Dorset SP8 4XL
Telephone: 0747822211
Telex: 417238 Aldrich G
FAX: 0747823779

Germany
Aldrich-Chemie GmbH & Co. KG
W-7924 Steinheim
Telephone: 07329870
Telex: 714838 Aldri D
FAX: 0732987139/239

Switzerland
Aldrich Chemie
Industriestrasse 25
P.O. Box 260
CH-9470 Buchs
Telephone: 08569723
FAX: 08567420

Australia
Aldrich Chemical
Unit 2
10 Ansett Ave.
Casele Park NSW 2154
Telephone: 028999977
FAX: 028999742



chemists helping chemists in research & industry

aldrich chemical co., inc.

P.O. Box 355, Milwaukee, Wisconsin 53201 USA

Telephone: (414) 273-3850
TWX: (910) 262-3052 Aldrichem
Telex: 26 843 Aldrich MI
FAX: (414) 273-4979

M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 5

PRODUCT #: 270520
MF: C4H8O2

NAME: ETHYL ACETATE, 99.8%, HPLC GRADE

CUST#: 100536
PO#: 58331-H

SCU-GPG LD50:3 GM/KG
TARGET ORGAN DATA

AGGHAR 5,1,33

SENSE ORGANS AND SPECIAL SENSES (OTHER OLFACTION EFFECTS)
SENSE ORGANS AND SPECIAL SENSES (CONJUNCTIVA IRRITATION)
LUNGS, THORAX OR RESPIRATION (OTHER CHANGES)
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES
(RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR
COMPLETE INFORMATION.

SECTION 12. - - - - - ECOLOGICAL INFORMATION - - - - -
DATA NOT YET AVAILABLE.

SECTION 13. - - - - - DISPOSAL CONSIDERATIONS - - - - -

BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND
SCRUBBER BUT EXERT EXTRA CARE IN IGNITING AS THIS MATERIAL IS HIGHLY
FLAMMABLE.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

SECTION 14. - - - - - TRANSPORT INFORMATION - - - - -

CONTACT ALDRICH CHEMICAL COMPANY FOR TRANSPORTATION INFORMATION.

SECTION 15. - - - - - REGULATORY INFORMATION - - - - -

REVIEWS, STANDARDS, AND REGULATIONS

ACGIH TLV-TWA 400 PPM 85INA8 5,239,86
EPA FIFRA 1988 PESTICIDE SUBJECT TO REGISTRATION OR RE-REGISTRATION
FEREAC 54,7740,89
MSHA STANDARD-AIR:TWA 400 PPM (1400 MG/M3)
DTLVS* 3,102,71
OSHA PEL:8H TWA 400 PPM (1400 MG/M3)
FEREAC 54,2923,89
OSHA PEL FINAL:8H TWA 400 PPM (1400 MG/M3)
FEREAC 54,2923,89
OEL-AUSTRALIA:TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL-BELGIUM:TWA 400 PPM (1440 MG/M3) JANUARY 1993
OEL-CZECHOSLOVAKIA:TWA 400 MG/M3;STEL 2000 MG/M3 JANUARY 1993

CONTINUED ON NEXT PAGE

Belgium
Aldrich Chemie
K. Cardonien, 8
B-2880 Bornem
Telephone: 038991301
FAX: 038991311

France
Aldrich-Chemie S.A.r.l.
B.P. 701
38297 Saint Quentin Fallavier
Cedex
Telephone: 74822800
Telex: 308215 Aldrich F
FAX: 74956808

Italy
Aldrich Chimica
Via Galvani, 154
20151 Milano
Telephone: 0233417370
FAX: 0238010737

Japan
Aldrich Japan
Kojima Bldg. Shinjuku
10 Kamida-Mura-cho
Chiyoda-Ku, Tokyo
Telephone: 0332580155
FAX: 0332580157

Spain
Aldrich Quimica
Apt. de Correos 161
28100 Alcobendas (Madrid)
Telephone: 3416619977
Telex: 22189 SAQ54
FAX: 3416618084

United Kingdom
Aldrich Chemical Co., Ltd.
The Old Brickyard, New Road
Gillingham, Dorset SP8 4JA
Telephone: 0747822211
Telex: 417238 Aldrich G
FAX: 0747823779

Germany
Aldrich-Chemie GmbH & Co. KG
W-7924 Steinheim
Telephone: 07329870
Telex: 714838 Aldrich D
FAX: 0732987139/239

Switzerland
Aldrich Chemie
Industriestrasse 25
P.O. Box 260
CH-9470 Buchs
Telephone: 08569723
FAX: 08567420

Australia
Aldrich Chemical
Unit 2
10 Anello Ave.
Castle Hill NSW 2154
Telephone: 028999977
FAX: 028999742



chemists helping chemists in research & industry

aldrich chemical co., inc.

P.O. Box 355, Milwaukee, Wisconsin 53201 USA

Telephone: (414) 273-3850
TWX: (910) 262-3052 Aldrichem
Telex: 26 843 Aldrich MI
FAX: (414) 273-4979

M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 6

PRODUCT #: 270520 NAME: ETHYL ACETATE, 99.8%, HPLC GRADE
MF: C4H8O2
CUST#: 100536
PO#: 58331-H

OEL-DENMARK: TWA 300 PPM (1100 MG/M3) JANUARY 1993
OEL-FINLAND: TWA 300 PPM (1100 MG/M3); STEL 500 PPM (1800 MG/M3)
JANUARY 1993
OEL-FRANCE: TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL-GERMANY: TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL-HUNGARY: TWA 400 MG/M3; STEL 1200 MG/M3 JANUARY 1993
OEL-JAPAN: TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL-THE NETHERLANDS: TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL-THE PHILIPPINES: TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL-POLAND: TWA 200 PPM JANUARY 1993
OEL-RUSSIA: TWA 400 PPM; STEL 200 MG/M3 JANUARY 1993
OEL-SWEDEN: TWA 150 PPM (500 MG/M3); STEL 300 PPM (1100 MG/M3) JANUARY 1993
OEL-SWITZERLAND: TWA 400 PPM (1400 MG/M3); STEL 800 PPM (2800 MG/M3)
JANUARY 1993
OEL-TURKEY: TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL-UNITED KINGDOM: TWA 400 PPM (1400 MG/M3) JANUARY 1993
OEL IN BULGARIA, COLOMBIA, JORDAN, KOREA, NEW ZEALAND, SINGAPORE,
VIETNAM CHECK ACGIH TLV
NIOSH REL TO ETHYL ACETATE-AIR: 10H TWA 400 PPM
NIOSH* DHHS #92-100, 92
NOHS 1974: HZD 31470; NIS 234; TNF 37072; NOS 152; TNE 407816
NOES 1983: HZD 31470; NIS 234; TNF 40728; NOS 154; TNE 504448; TFE
119505
EPA GENETOX PROGRAM 1988, INCONCLUSIVE: B SUBTILIS REC ASSAY
EPA TSCA CHEMICAL INVENTORY, JUNE 1990
ON EPA IRIS DATABASE
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JANUARY 1993
NIOSH ANALYTICAL METHODS: SEE ETHYL ACETATE S49

SECTION 16. - - - - - OTHER INFORMATION - - - - -

THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. ALDRICH SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR PACKING SLIP FOR ADDITIONAL TERMS AND CONDITIONS OF SALE.

CONTINUED ON NEXT PAGE

France
Aldrich-Chemie S.a.r.l.
B.P. 701
38297 Saint Quentin Fallavier
Cedex
Telephone: 74822800
Telex: 308215 Aldrich F
FAX: 74956808

Japan
Aldrich Japan
Eiyodo Bldg. Shinjuku
10 Kanda-Miduracho
Chiyoda-Ku, Tokyo
Telephone: 0332580155
FAX: 0332580157

United Kingdom
Aldrich Chemical Co., Ltd.
The Old Brewery, New Road
Gillingham, Dorset SP8 4L
Telephone: 0747822211
Telex: 417238 Aldrich G
FAX: 0747823779

Switzerland
Aldrich-Chemie
Industriestrasse 25
P.O. Box 350
CH-9470 Buchs
Telephone: 08569773
FAX: 08567420

Germany
Aldrich-Chemie GmbH & Co. KG
W-7974 Steinheim
Telephone: 07329870
Telex: 714838 Aldrich D
FAX: 0732987139/239

Australia
Aldrich Chemical
Unit 2
10 Aranda Ave.
Castle Hill NSW 2154
Telephone: 028999977
FAX: 028999742

TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, Micro-Electro-Mechanical Systems (MEMS), and data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and composites; development and analysis of advanced materials processing and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle fluid mechanics, heat transfer and flight dynamics; aerothermodynamics; chemical and electric propulsion; environmental chemistry; combustion processes; spacecraft structural mechanics, space environment effects on materials, hardening and vulnerability assessment; contamination, thermal and structural control; lubrication and surface phenomena; microengineering technology and microinstrument development.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.